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FINAL REPORT TO THE

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Project title:

Studies of the interrelation of hide quality with the rate of tanning and the efficiency of tanning to obtain information for use in developing improved processes for making leather.

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C O N T E N T S

SUMMARY

The quality of raw hides depends on a number of factors like feed, breed, age, care of the living animal, flaying and curing etc. The variations in hide quality reflect directly on the finished leathers. Adequate knowledge is not available to determine the hide quality and correlate the hide quality with finished leather quality. Hence, a detailed study was made on some of these factors that affect quality. First, a new method was developed to assess hide quality. Then the influence of (a) interfibrillary matter (b) locational variations in thickness and structure, (c) cause of death of the animal (i.e. hide obtained from slaughtered and fallen animal) (d) curing, delays in curing, certain pretanning operations (e) the rate of penetration of tannin on the final quality of leather from cow and buffalo hides were studied and reported here.

A new method was developed for the quantitative determination of the extent of deterioration in hide quality during staling or during long storage based on the estimation of extractable hydroxyproline present in soak liquor. As no quantitative method was readily available for the determination of hide quality the present method may find considerable use in future investigations.

A study on the protein and carbohydrate constituents of the interfibrillary materials of cattle hide was made with a view to find out their influence on the properties of finished leather. The protein constituents were found to vary in different locations of cattle hide. Extractable salt soluble proteins were mostly removed but about 35% of extractable lime soluble proteins was found to be retained by the pelt after pretanning operations. The non-protein constituents and tyrosine of salt soluble and lime soluble extracts of cattle hide were also quantitatively determined. Small proportions of these components appeared to be unextractable by salt and lime extraction. Influence of interfibrillary materials on the properties of finished leathers is possibly due to the constituents which are extractable by lime but are retained by the pelt after usual beamhouse treatments.

But a precise knowledge about the composition of this fraction of lime soluble materials and its influence on the properties of leather is yet to be acquired.

Effects of thickness and structural variation in hide on the rate of chrome and vegetable tanning were studied. Rate of tanning and physical properties of the leathers were found to be affected due to these variations. The influence of delay in cure, precuring extraction of hide with sodium chloride and half saturated lime, various types of cure and pretanning operations on the rate of vegetable tanning, sole leather yield and on physical properties of the leathers from buffalo hide were determined in laboratory scale experiments. The data obtained from these investigations may significantly help in improving or modifying tanning processes and to achieve better properties of sole leathers.

The leather making properties of fallen and slaughtered cattle and buffalo hides collected from different sources and from different regions ofIndia were studied. Cattle hides were finished into full chrome upper leathers and buffalo hides into vegetable tanned sole leathers. Slaughtered cattle and buffalo hides collected from slaughter houses and the leathers produced from them were found to be better in quality than the fallen hides collected from Flaying and Carcass Utilization Centres and the leathers obtained from them. Market quality slaughtered and fallen cattle hides and the leathers made from them were found to be comparable to each other. But in case of market quality buffalo hides, slaughtered hides graded better than fallen hides. Flint dry fallen hides were much poor in quality and most of them were not suitable for full chrome upper leather. Physical properties of chrome upper leathers from slaughtered and fallen hides were analysed statistically and were compared. It was, however, observed in general that the leather making potentialities of slaughtered and fallen hides belonging to the same grade in raw classification were not affected to any appreciable extent.

The present investigation further revealed the basic factors that were responsible for the deterioration of both fallen and slaughtered hides. Fallen hides were degraded in quality due to microbial action during staling, mechanical damage, congealed blood patches, inadequate cure and long storage; slaughtered hides, on the other hand, suffered from flaying defects, old age, etc. Both the slaughtered and fallen hides were affected due to tick, pock and vein marks and poor flanks. The present work points out that there is considerable scope of improvement of the qualities of both slaughtered and fallen hides, particularly of fallen hides.

The efficiency of flint dry, frame dry and dry salted cattle hides for the production of chrome upper leather was examined in comparison to control wet salted hides. Frame dry hides were found to yield leathers roughly comparable to that of control leathers. For the preparation of dry hides the superiority of frame drying method was confirmed.

An effort was made to find out a better way of utilising the buffalo hide offals (medium weight) i.e. shoulder and belly pieces. They were converted into six different types of leathers and an assessment of value index showed that the production of banwar and kattai leathers was more prospective.

INTRODUCTION

1. Hides and skins, the basic raw materials for the leather industry, deteriorate in quality due to a number of antemortem and postmortem defects. As these defects in hides and skins obtained from various sources are quite different in nature, it has not been possible to standardize any unilateral method for the assessment of hide quality. A good number of these defects are, however, visible and can be recognised by careful inspection but the defects which are invisible, create considerable problem in hide assessment. Factors like breed, age, living conditions and cause of death of the animal have limited deteriorating effect on hide quality, but a hide may completely lose its leather making potentiality depending on the extent of delay in cure, inadequate cure and long storage period. The effect of delay in cure on hide quality has therefore been well emphasised from time to time by different investigators[1,2,3,4,5].

Commercial hides and skins are generally cured by wet salting or brining method whereby the hide absorbs about 15 percent salt and loses about 20% water. Chemical analysis of wet salted hide for salt and moisture has been the most common trade practice to get first hand information about the proteinous substances present in the hide. Although this method can give a rough account of the non-leather making substance present in the hide it does not indicate the quality of the hide. The histological method[6] of assessing hide quality was adopted by many investigators either alone or along with other chemical methods. But this yielded only an assessment of qualitative measure. Whitmore et al[7] were of opinion that extractable nitrogen in cured hides, if present above 5% level, shall indicate deterioration in hide quality. Somer[8] correlated the volatile nitrogen content of heavy cured hides with tannery yield of leather and found that a well cured hide could yield upto about 0.3% volatile nitrogen. But the limitations of the above methods were pointed out by Hauck and Lollar[9]. Different other approaches were also made to evaluate hide quality based on the estimation of free fatty acid[10], total amino acid nitrogen[11], specific amino acids[12], lactic acid[12], aldehydes[12] and so on. A measure of the percent contraction in length of collagen fibre after 2 mt. treatment in 0.13 N HCl was considered by Volpert[13] to give an indication of the hide quality.

It was observed[3] that bacteria first attacked the interfibrillary proteins and made their way into the hide structure and then became active against fibrous proteins. The basic leather making substance in hides and skins is collagen. It has therefore been considered that an estimation of hydroxyproline present in the hide would give an account of the leather making potentiality of the hide. But the effect of microbial deterioration of hide on its hydroxyproline content is not known with certainty. Based on the action of proteolytic enzymes present in fluid extracted from hide on photographic gelatin film, Schmitt and Deasy[14] suggested a method for estimating the delay in cure. Such an assessment is, however, qualitative in nature. As there is no convenient quantitative method to study the quality of raw hide and the extent of deterioration that has taken place in the hide, a further investigation in this field is considered necessary.

2. Besides fibrous protein, raw hides contain small amounts of interfibrillary proteins. Of these albumins (water soluble) and globulins (salt soluble) are generally termed as globular proteins or coagulable proteins. During salt preservation, certain amounts of globular proteins get denatured. Considerable amount of globular proteins and probably some mucoproteins undergo denaturation when hides are dried in the hot sun and this is mainly responsible for the problem of rewetting dry hides. It was observed by different investigators[15,16,17] that wet salted calfskins after soaking retained certain amount of globular proteins. Pandit and Roddy[18] noted that the extraction of coagulable protein nitrogen was the minimum in case of flint dry skins.

Mucoids and mucopolysaccharides which are extractable by half-saturated lime liquor, are partially removed during beamhouse operations. Schneider[19] observed that albumins, globulins and also mucoids present in the skin were degraded and dissolved by trypsin. A good amount of interfibrillary matters were found to be removed by enzyme bates[20,21,22]. Burton, Reed and Flint[23], however, pointed out that the removal of mucoid material was basically responsible for soaking back, unhairing and bating of hide.

According to Cooper and Johnson[24] the major constituent of the ground substance of the skin was similar to plasma proteins. The presence of an albumin like glycoprotein in calf skin was reported by Got and Bourrillon[25]. The presence of non fibrous proteins in hides and in pelts to different extent was considered by different investigators[15,26,27] to have certain influence on processing and on the properties of leather. The presence of the globular proteins, particularly in the epidermal or grain area, may affect the grain characteristics of finished leathers. But precise information regarding the presence of these interfibrillary proteins in pelt just before tanning and their influence on the quality of the finished leather is rather limited.

According to Meyer[28] mucoids are classified into three main groups (i) mucopolysaccharides, (ii) mucoids and (iii) glycoproteins. Mucoids and glycoproteins are both amino sugar protein complexes differing only in the amount of amino sugar present in them. Globular proteins also contain different glycoproteins. Following the fractionation technique of Meyer and Chaffee[29] the acid mucopolysaccharides e.g. hyaluronic acid and chondroitin sulphate of the calf skin[30] and bull skin[31] were isolated. Recent studies[32,33,34,35] contributed more quantitative data on the monosaccharide units of the mucopolysaccharides in skin. It is, however, important to have a better understanding about the carbohydrates which are present merely as constituents of the ground substance and those which are in some way combined with the fibres. Analysis of the interfibrillary materials extracted by salt solution and half-saturated lime solution for non-protein constituents will provide further information about the composition of interfibrillary substances present in hides.

3. The rate of diffusion of tannin materials in hide or in pelt depends on a number of complicated factors of both chemical and physical nature. Mezey[36] investigated the rate of penetration of different tannin materials. He[37] pointed out that this rate of penetration might be influenced by the concentration, astringency, pH of the tan liquor, presence of electrolytes in it etc. Stather[38], observed that temperature and pH of both hide and liquor affected the rate of tannin penetration. He further noted that tannin penetration was also roughly proportional to the square root of time. In a later study Stather and Herfeld[39] reported that rate of tanning, tannin fixation and degree of tannage increased with rise in temperature. According to Pawolowitsch[40] diffusion of tannin was maximum in the pH range 7 to 8 but its fixation was minimum in this range of pH. The effect of neutral salt concentration on the rate of tanning by hemlock and gambier at different pH levels was studied by Thomas and Kelly[41]. A survey of the literature revealed that a considerable amount of work had been done covering various chemical aspects but information about the effect of physical factors on the rate of tanning are rather limited.

It was pointed out by Braybrooks et al[42] and supported by Kremen and Lollar[43] that the swelling of raw collagen might considerably influence the rate of tanning. Sykes[44] studied the effect of swelling of untreated, deaminated, acetylated, esterified and formaldehyde treated hide samples on the fixation of tannin and observed a general trend of increased tannin fixation with increased swelling of collagen.

A variation in hide quality may also influence tanning rate and also the quality of finished leather. Such difference in hide quality may be caused by factors like areawise variation in hide due to thickness and structural changes, delay in cure, extraction of hide prior to curing or tanning, methods of curing and so on.

Structural variation in cattle hide can hardly be modified but variation in thickness may be eliminated by splitting the hides during upper leather manufacture. Splitting is done either in the 'lime' or in the 'blue' stage. Lime splitting may be advantageous[45] in certain respects e.g. the splits may be processed as desired, slight gain in area yield, reduction of cost of materials and reduction of processing time. On the other hand, it was reported[46] that hides splitted in blue stage produced leather of tighter grain. Moreover, splitting seems to be comparatively easier when operated in blue stage. The influence of areawise variation in hide on the rate of chrome tanning and the effect of lime splitting on the qualities of chrome upper leather may be investigated.

Holmes and Wollenberg[47] demonstrated that thickness of hide affectedthe rate of tanning and in thinner areas the rate of tanning was quicker. Besides thickness, the compactness of the hide or pelt may also influence the rate of vegetable tanning. A study on the effect of areawise variation in buffalo hide on the rate of vegetable tanning and on the qualities of sole leathers would thus be of considerable importance.

Delay in cure may affect the quality of hide which in turn may influence the rate of vegetable tanning. Two large scale experiments were conducted by the British Leather Manufacturers' Research Association[48] in conjunction with Penketh and Camden Tanning Companies with hides staled for 3 to 14 days. Leathers produced from staled hides were affected by grain damage but had little change in physical properties. Stather and Sluyter[49] reported that white weight gain and leather weight yield did not vary between fresh and 24 hr. staled hide (staled at 18°C), cured either by salting or brining. In a later study, Stather and Herfeld[2] extended the staling period to 72 hr. and observed no variation in leather yield, specific gravity, tensile strength, stretch and chemical composition between fresh and staled hides. Leathers produced from 72 hr. staled hide were, however, spotted in the grain and absorbed more water than other samples. It is well recognised that the intensity of the effect of delay in cure depends to a great extent on the temperature[5,10] during staling and in a tropical country like India, staling may have more pronounced effect on leather quality than in cold climatic regions. Moreover, a good proportion (>80%) of the Indian buffalo hides are obtained from fallen animals which often undergo staling for a period of 24 hr. or even more. A study on the effect of staling on the leather making property of buffalo hide is expected to throw considerable light on this aspect.

According to Roddy[15] globular proteins present inside the hide might affect the diffusion of vegetable tanning liquors. He noted that a fresh hide when extracted with salt solution for 24 hr., stored for 30 days after salt curing and then tanned using quebracho extract could produce a plumper and heavier leather. On the other hand, incomplete removal of denatured globular proteins during beamhouse operations resulted in lower leather yield. Whether removal of interfibrillary proteins by extraction prior to curing/or tanning increases leather yield and influences the properties of sole leather may be examined.

McLaughlin and Theis[50] reported that heavy hides cured by brining produced thicker and firmer leather with higher leather yield than green salted hides. A higher white weight gain and equal or better leather yield by heavy brined hides was also noted by DeBeukelaer[51]. Whether similar trend of variation do exist in case of buffalo hide of lower weight range may be verified. In certain tanneries hides are bated and then vegetable tanned. Bating is expected to help complete deliming and to improve the general appearance of the finished leathers but the effect of bating on the rate of tanning, on leather yield and on properties of the leather are not known with certainty. Hides may be unhaired enzymatically[52] to prepare pelt for tanning even without prior alkaline swelling. It would also be interesting to know how the enzyme unhaired buffalo pelt behaves towards rate of tanning, and on other properties of sole leather. It is also possible that sole leather yield may be affected if the hide is cured in different ways e.g. air dried, dry salted, etc. But published report in this respect is rather insignificant. The influence of the above variations in hide quality on the rate of tanning and on the properties of sole leather may thus be elucidated in the present investigation.

4. Establishment of the inter-relation of hide quality to the efficiency of tanning or to the quality of finished leather is of critical importance but has attracted attention of the technologists only in recent years. This is probably due to the complicated nature of the problem as the variation in hide quality may not always influence directly the commercial qualities of the leathers or their physical and chemical properties. Many studies regarding the relationship between hide and leather quality might have been conducted either in laboratory or in plant scale but very few of them were reported.

It is well established[53] that the structure of hide or skin greatly influences the properties of finished leather. That the breed of the cattle, the environmental living conditions and age of the cattle affect the structural characteristics of the hides and in turn the leather quality is also well recognised. The effect of delay in cure on the quality of raw hide and consequently on shoe upper leather quality was studied by Hauck and Lollar[9] with a view to establish some correlation between the properties of raw hides and finished leathers. It was noted that physical strengths of the leathers might depend on the amount of the protein present in the hide. Combs et al[54] studied the leather making characteristics of calf skins which were obtained (i) by skinning immediately after slaughter of the animal and (ii) by removing the skin in the cooler after permitting the skin to remain on the carcasses for some time. The qualities of the finished leathers were, however, found unaffected although some correlation of the strength of the raw stock to that of the finished leather was noted. In a later study Fopma et al[55] attempted to find out a positive relationship between the chemical composition of the hide and the physical strength of the leather. Although it was not possible to establish such a relationship, it was observed that mullen grain strength and slit tear strength were significantly lower in leathers from cull lots of hides than for the leathers obtained from hides of small packer lots. No correlation was found by Ornes and Roddy[56] between the chemical characteristics of green salted hide and the physical strength of the finished leather.

In most of the countries cattle hides are obtained as by-products of slaughter houses while a small percentage of the hides is obtained from fallen animals. In Denmark, hides from dead animals are marketed along with the hides from slaughtered animals depending on their quality. In England, fallen hides are sold separately and they fetch much lower price than slaughtered hides. In India, on the other hand, about 86% of the available cattle hides[57] are obtained from dead animals and are marketed with the slaughtered hides according to their quality. Cattle may die suddenly due to certain disease when the quality of the hide may not be deleteriously affected but when the animal dies a natural death due to old age, the quality of the hide may be comparatively poor. Even after the death of the animal flaying and curing may be either delayed or are poorly done. It is quite apparent that the leather making potentiality of each hide will entirely depend on the extent to which it has suffered deterioration and damage before it is actually processed. Slaughtered hides may also be affected in quality due to certain factors. Moreover slaughtered hides obtained from hide markets are not always collected from slaughter houses but also from private butchers in the country side. But no report has been published investigating the inherent quality of the fallen hides and their relationship to the quality of the leathers produced in comparison to that of slaughtered hides. A comprehensive study has therefore been undertaken to study the qualities of upper leathers from fallen and slaughtered hides collected from different sources. Besides these the leather making property of fallen hides available in flint dry condition has also been included in this study.

Drying of hides and skins in the sun or shade is the simplest and most economic way of curing them. Because of different problems e.g. difficulty to rehydrate, insect damage and problem of quality assessment, associated with dry hides they are not generally preferred by the tanners. Rehydration of dry hides may be improved by using modern methods of drying[58,59] and by using certain soaking agents during soaking of dry hides. Insect damage may also be reduced by treating the hides with effective insecticides. Data are, however, limited about the comparative leather making properties of the dry, dry salted and wet salted hides and warrant further investigation in this field.

Like that of cattle hides about 87.0%[57] of buffalo hides are obtained from dead animals. As there is no published report about the qualities of fallen buffalo hides and their relationship to the qualities of sole leathers a study has been undertaken comparing the leather making properties of fallen and slaughtered buffalo hides. The other problem precipitating in India is the proper utilisation of buffalo hide offals like shoulder and belly pieces. Although marketing hides into croupon, shoulder and belly is a common practice in Europe and U.S.A., hides are marketed in India only in full pieces. The bends of heavy buffalo hides are often used for certain types of industrial leathers but to process the offals and to market them effectively is often a difficult task for some of the tanners. It is thus thought to exploit the various possibilities of utilising the offals in a prospective way so as to get higher market values.

CHAPTER I.

1. Evaluation of raw hide quality.

In the present work an attempt was made to find out the inter-relationship between the extractable hydroxyproline and the quality of fresh or salted hide and to use extractable hydroxyproline as an index for the quality of hide.

2. Methods.

2.1. Estimation of hydroxyproline.

Hide pieces were first dehaired with a razor, dehydrated with acetone, powdered, hydrolysed in a sealed tube with 6N HCl at a temperature of 105°C for 18 hrs. and then made up to a volume with distilled water. Hydroxyproline was then estimated by Newman and Logan method[60] and expressed as per cent on moisture free hide.

To determine the hydroxyproline content of soak water an aliquot of 25 ml. of soak water was taken in a sealed tube, digested with conc HCl and then dried over water bath. The dried hydrolysate was next dissolved in distilled water, made upto a known volume (100 ml.) and filtered. Hydroxyproline was then estimated as before.

2.2. Tyrosine in soak water.

Acid hydrolysed soak liquor that was used for the estimation of hydroxyproline was taken for tyrosine estimation. Extractable tyrosine present in dfferent soak liquors obtained from salted hides was studied and determined by a colorimetric method[61] and expressed in terms oftyrosine as per cent of total nitrogen.

2.3 Total nitrogen.

Total hide nitrogen was estimated by digesting about 1g. of hide sample with sulphuric acid and then estimating the nitrogen by Kjeldahl method.

2.4. Extractable nitrogen.

Another aliquot of 25 ml. soak water was taken, digested with sulphuric acid and nitrogen was estimated by Kjeldahl method. Extractable nitrogen is expressed as percentage of total nitrogen.

2.5. Procedure for chrome tanning.

Based on preliminary trials a method for the manufacture of full chrome shoe upper leather was standardised and was followed throughout the investigation.

Wet salted cattle hides were cut into sides, washed to remove excess salt and soaked overnight in a pit containing sufficient amount of water. Next morning the hides were green fleshed if necessary, excess water was allowed to be drained out. The hides were then weighed.

The lime liquor was composed of the following: sodium sulphide (60%) - 2.25%, ammonium sulphate - 0.5% and water 300-350% (all on soaked weight). The sides were handled in the above bath for about 10 mt. and then 3% slaked lime was added to it. Liming continued for two days and the sides were handled in the liquor thrice in a day. On the third day they were unhaired, fleshed, scudded and then weighed (pelt weight). Limed pelts were then delimed with 0.75% ammonium sulphate (or 0.5% ammonium chloride) and 150% water (on pelt weight). Because of the comparatively poor quality of raw cattle hides bating was not considered absolutely necessary and so bating operation was excluded.

During pickling, the pelts were run for 5 mts. in a drum with 5% salt and 80% water and then 1.25% sulphuric acid (1.04 sp. gr.) was added in diluted form in thin stream. The drum was run for 1 hr. and the pelts were left overnight in the pickle bath. Next morning drumming was continued for 30 mts. and the pH of liquor was checked to be 2.8 - 2.9.

The pickled pelts were run in the drum with 2% salt and 80% water. Chrome liquor was prepared in the previous day by dissolving 7% chrome extract powder (25% Cr_2O_3, 33% basic) on pelt weight in 20% water at 60°C. Chrome liquor was then added to the drum in one feed. The drum was run for 3 hrs. The liquor was then basified with 0.5% sodium bicarbonate added in two instalments. The tanned pelts were taken out and piled overnight. Final pH of the liquor was checked to be 3.5. - 3.6. Next day the leathers were sammed, shaved (splitted if necessary) and then weighed (shaved weight).

The leathers were again drummed for 10 mt. with 25% water and then 3% chrome extract powder (on shaved weight) dissolved in 25% water and made 50% basic by addition of soda ash, was fed into the drum. The drum was then run for 30 mt. and the tanned leathers were horsed up overnight.

The leathers were then washed and neutralised in a drum with 0.75% sodium sulphite and 125% water for 45 mt. The pH on the surface of the leather should be about 4.5 - 4.6 and in the centre about 3.7-3.8. The leathers were then dyed with 0.75-1% acid dye and 125% water at 60°C. Dyed leathers were then fat liquored with a mixture of 1.75% sulphated fish oil and 0.5% groundnut oil emulsified in 25% water. After drumming for 20 mt. 1% gambier extract was added to the drum. After another 20 mt. drumming 0.25% formic acid was fed into the drum and run for another 10 mt. The leathers were then taken out of the drum and horsed up. Next day the sides were sammed and oiled lightly on the grain. They were set out and dried. Crust leathers were conditioned under saw dust and then staked and toggled on boards for drying. Dried leathers were trimmed, buffed on the flesh side and then finished with casein finish.

2.6. Visual assessment of leathers.

Finished leathers were assessed for quality by visual inspection depending on general appearance, smoothness of grain, temper, tightness and grain break, grain crackiness and fullness of shanks. Leathers were assessed by a reputed tanner into first, second, third and rejection quality but this classification may differ from commercial grading of the leathers.

2.7. Physical properties of leather.

Samples were taken from the sampling position (Fig. 1) of each side (both control and experiment 1) and certain physical properties were determined. Tensile strength, elongation, stitch tear strength and tongue tear strength were determined by a Scott Tester

(Model J); grain cracking and bushing strength were determined by a Mullen Tester.

3. A new method for the determination of hide quality.

3.1. Experimental procedure and results.

3.1.1. Extractable hydroxyproline in staled hides.

A freshly slaughtered cattle hide was collected, washed to free from blood and manure and the adhering fat, flesh, etc., were removed. Experimental pieces were then cut out from the butt area. Hide pieces were allowed to be staled at a temperature of 28 ± 1°C for different periods.

In one case staled hide pieces were taken in distilled water(1:5) and soaked for 1 hr. with occasional hand shaking. The soak water was then filtered through filter cloth with thorough washing and made up to volume.

In the other case, hide pieces staled for different periods were salted with 40% salt on green weight and kept in a pile. After two weeks, the hide pieces were shaken free of excess salt and soaked separately in distilled water for 1 hr. The soak liquors were then filtered and made up to volume.

Hydroxyproline and nitrogen contents of the soak liquors were estimated. Tyrosine was estimated in soak liquors obtained from salted samples.*

It is apparent from the results in Tables I and II that the hydroxyproline content of the hide remains practically unaffected irrespective of the deterioration of hide during staling. An estimation of the hydroxy-proline content of hide is thus unable to give a correct indication of the quality of hide.

Extractable nitrogen in fresh hide increases with the increase in staling period. Values for extractable nitrogen are found to differ between unsalted and salted hides. The values for unsalted hides are less up to 24 hr. staling but become higher as compared to values for salted hides on further staling. This is

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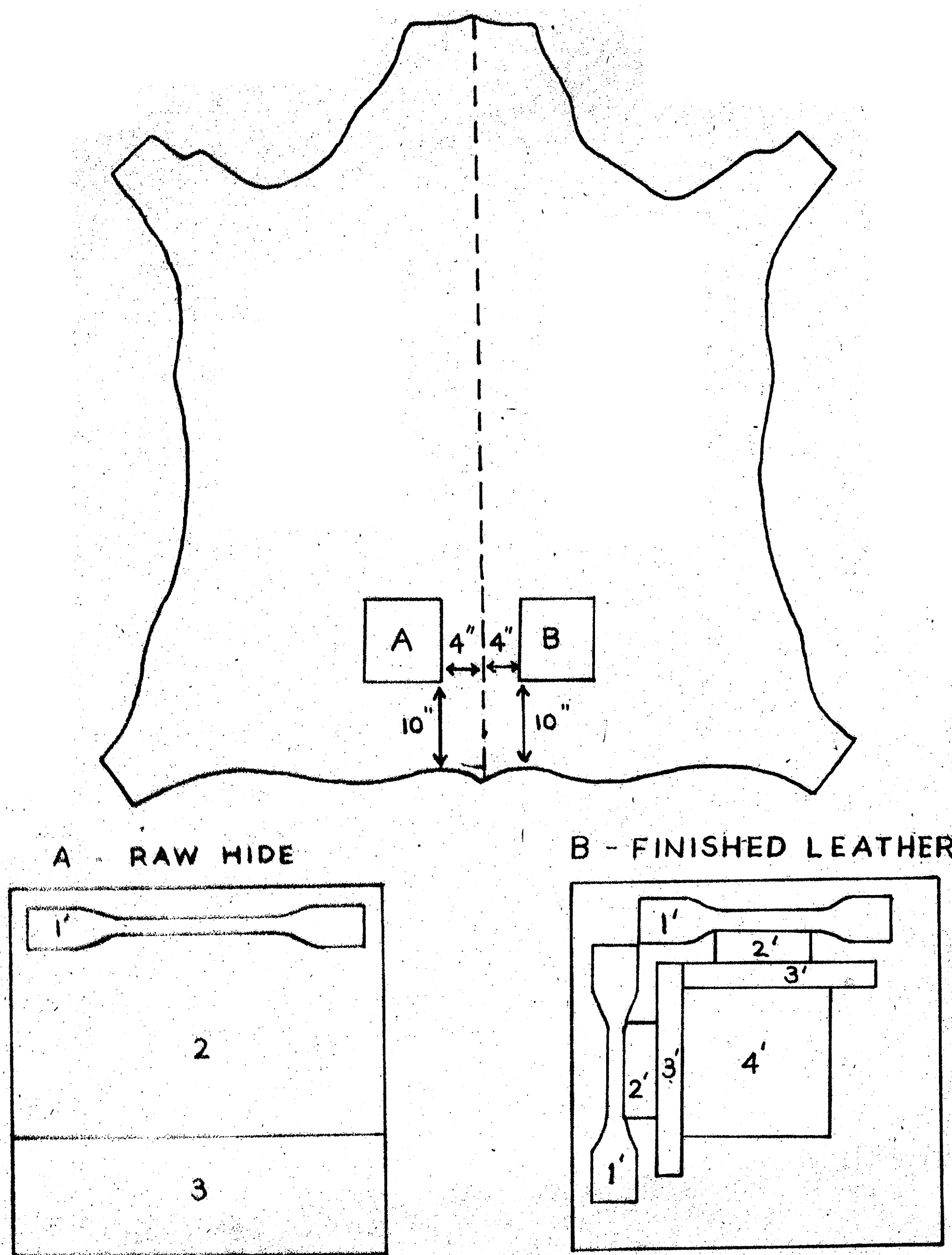
* Tables I and II comprise with the data on hydroxy-proline, extractable N and extractable hydroxyproline N in cases of unsalted and salted samples.

FIG. 1



1 - TENSILE STRENGTH
2 - CHEMICAL ANALYSIS
3 HYDROXYPROLINE

1 & 1' - TENSILE STRENGTH
2 & 2' - STITCH TEAR "
3 & 3' - TONGUE TEAR "
4 - BURSTING STRENGTH.

TABLE I

Extractable hydroxyproline and nitrogen in unsalted staled hide

Period of staling (hours)	Hydroxy-proline of staled hide (% of moisture free hide)	Extractable N (% of total N)	Extractable hydroxyproline N			Extractable collagen N (% of total N)
			(% of total N)	(% of extractable N)	(% of hide hydroxy-proline)	
Fresh	10.39	0.23	Nil	Nil	Nil	Nil
16	10.41	0.53	Nil	Nil	Nil	Nil
24	10.52	0.73	Nil	Nil	Nil	Nil
40	10.71	3.16	0.017	0.52	0.009	0.20
48	10.81	8.16	0.046	0.57	0.024	0 .57
64	10.89	11.48	0.069	0.60	0.037	0.86

TABLE II

Extractable hydroxyproline and nitrogen in salted staled hide

Period of staling (hours)	Hydroxy-proline of staled hide (% of moisture free hide)	Extractable N (% of total N)	Extractable hydroxyproline N			Extractable collagen N (% of total N)
			(% of total N)	(% of extractable N)	(% of hide hydroxy-proline)	
Fresh	10.51	0.53	Nil	Nil	Nil	Nil
16	10.88	0.72	Nil	Nil	Nil	Nil
24	10.64	1.19	Nil	Nil	Nil	Nil
40	10.78	2.73	0.02	0.78	0.01	0.26
48	10.73	5.93	0.05	0.88	0.03	0.64
64	10.82	7.11	0.07	1.04	0.04	0.91

probably because of the fact that considerable amounts of soluble proteins produced in highly staled hides due to bacterial action are drained away along with the brine during salting.

Results on extractable hydroxyproline point out that hydroxyproline is practically unextractable up to 24 hrs. staling under the experimental conditions. With further staling, however, hydroxyproline is extracted progressively. There is only slight variation in extractable hydroxyproline content in salted and unsalted hides. Although extractable hydroxyproline nitrogen may be expressed in different ways, results expressed as per cent of total nitrogen are more reliable.

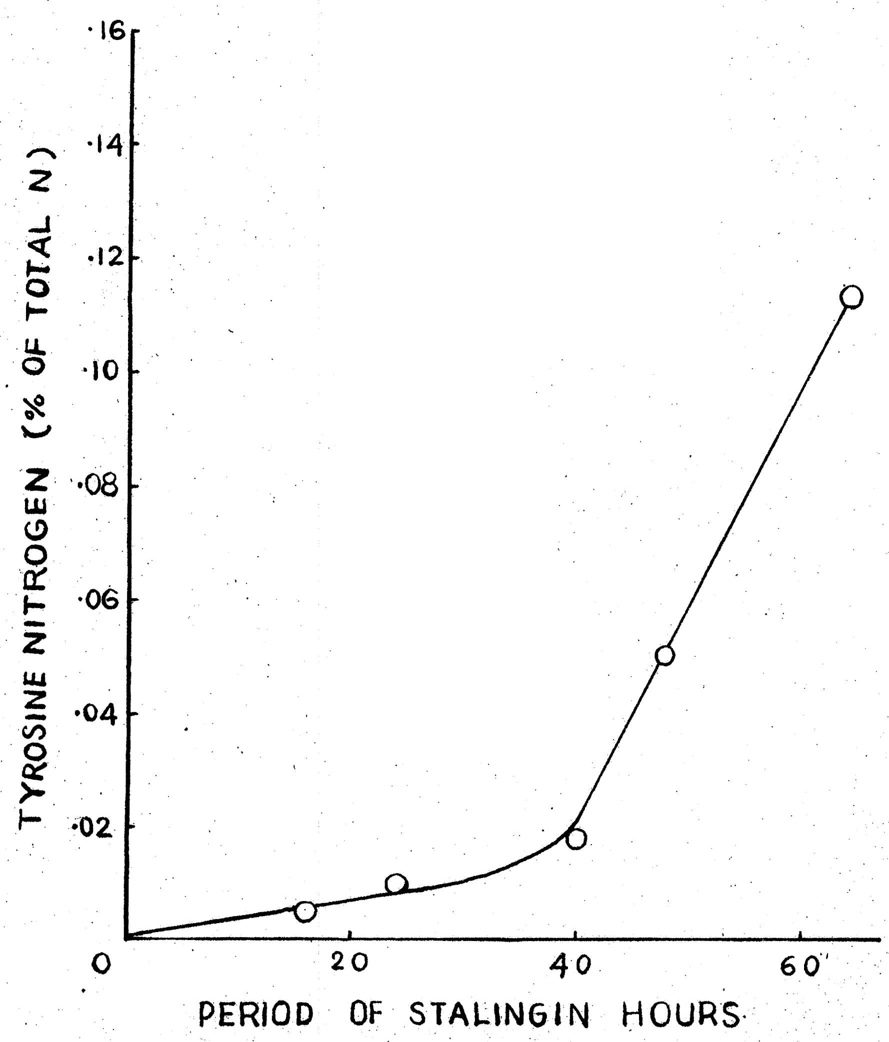
The increase in tyrosine content in soak water obtained from salted hides which were initially staled for different periods is presented in Fig. 2. Tyrosine is found to be present only in traces in soak water from fresh hide and increases slowly up to 24 hrs. staling and then increases progressively with further increase in staling. The low tyrosine content in the first few soak liquors obtained from less staled hides is probably due to the extraction of tyrosine containing proteins along with brine during salting.

Tyrosine is present mostly in globular proteins of hide and the data obtained thus point out that globular proteins are also degraded to a greater extent only after a staling period of about 24 hrs.

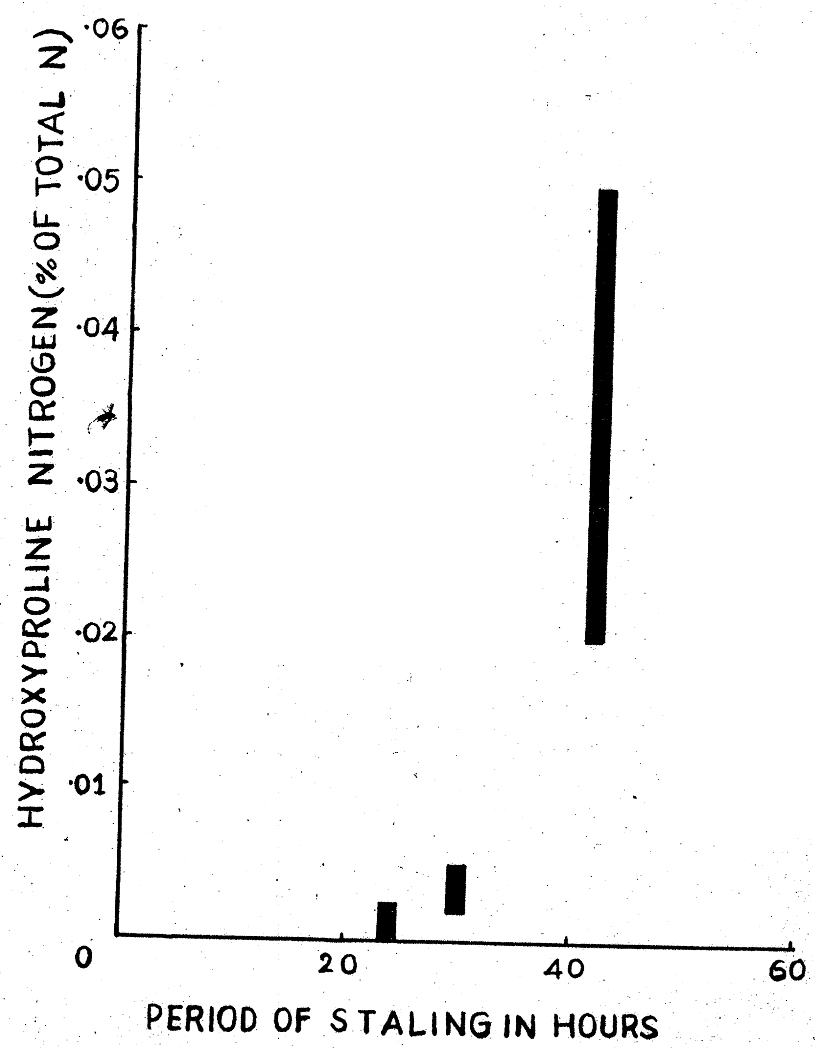
3.1.2. Locational variation.

It is quite possible that extractable hydroxyproline content may vary in different areas of the hide. Extractable hydroxyproline was thus determined in different parts of the hide and after different periods of staling.

A freshly slaughtered cattle hide was taken andcut into two sides, one side was washed well with water and the other side was left unwashed. Samples were then cut from different areas of the sides e.g., butt, belly, shank and neck. These were then allowed to stale at



·16
·14
·12
·10
·08
·06
·04
·02
0
20
40
60
TYROSINE NITROGEN (% OF TOTAL N)
PERIOD OF STALINGIN HOURS


HYDROXYPROLINE NITROGEN (% OF TOTAL N)
·06
·05
·04
·03
·02
·01
0
20
40
60
PERIOD OF STALING IN HOURS

$30 \pm 1^{o}C$ for different periods. After desired staling periods, each hide piece was soaked separately and the hydroxyproline content of soak liquor was estimated as before, The ranges of variation in extractable hydroxyproline as presented in Fig. 3 are obtained from the analyses of 8 samples (4 washed and 4 unwashed) in each case.

As in previous occasions no hydroxyproline is found to be present in soak liquors obtained from fresh and 16 hr. staled hides. Practically no hydroxyproline is found to be present in case of washed and 24 hr. staled hide pieces but in unwashed hides, a small quantity of hydroxyproline is found to be extracted. Slight 'hair-slip' is also noted in unwashed hide after staling for 24 hr. whereas washed hide demonstrated practically no 'hair-slip' after the same period of staling. This shows that washing of the hide may help to some extent in delaying its deterioration during staling. But as the staling period proceeds further no distinction can be made between washed and unwashed hides in respect of hydroxyproline extraction or 'hair-slip'. The range of variation is also broad after 42 hrs. of staling.

3.1.3. Effect of soaking period.

The period of soaking may have certain influence on hydroxyproline extraction and the extent of such variation was examined in the following experiment.

Fresh washed hide samples were staled for 28 hrs. at $30 \pm 1^{o}C$ and then salted with powdered salt. Slight 'hair-slip' was noticed in salted hide samples. Experimental samples were then cut into small pieces (2.5 Sq. inch) mixed together and divided into four lots, each weighing approximately the same. They were then soaked in distilled water in the following ways (i) soaked for 1 hr. with occasional hand shaking, (ii) soaked for 2 hr. with occasional hand shanking, (iii) soaked for 1 hr. in a mechanical shaker and (iv) soaked for 3 hr. in a mechanical shaker. Chloroform and toluene were added to the soak liquor used for 3 hr. soaking. As before, nitrogen and hydroxyproline present in soak

TABLE III

Effect of period of soaking on hydroxyproline and nitrogen content of soak liquor

Condition of soaking	Period of soaking	Extractable hydroxy-proline N	Extractable collagen N	Extrac-table N
			% of total N	
Shaken occasionally by hand	1 hour	0.004	0.05	1.94
"	2 hours	0.004	0.05	2.23
Shaken in a mecha-nical shaker	1 hour	0.004	0.05	2.08
"	3 hours	0.004	0.05	2.56

TABLE IV

Effect of drying of salted hide on hydroxyproline and nitrogen content of soak liquor

Extent of drying	Moisture content of hide (%)	Extractable hydroxyproline N	Extractable collagen N	ExtractableN
		(on initial wet salted wt. basis; % of total N)		
Wet salted	39.27	0.029	0.36	5.84
Partially dried	34.58	0.029	0.36	6.96
Dry salted	21.77	0.028	0.35	5.18

liquors were determined. Results are given in Table III.

The results indicate that the period of soaking does not considerably influence the extraction of hydroxyproline from the hide. For practical purposes, soaking for a period of 1 hr. in a mechanical shaker may be considered sufficient to be followed as standard practice for other experiments.

3.1.4. Effect of dehydration.

Often the salted hides are dehydrated to different extents during storage and transport. The effect of drying of the hide on hydroxyproline extraction was thus studied.

Freshly slaughtered hide sample was staled for 42 hr. at 30°C and then salted. After about 3 weeks' storage, excess salt was shaken off the hide and the moisture content was determined. This was then cut into two pieces, weighed and dried to different extents in the laboratory. Moisture was determined in each case. Wet salted hide pieces were then soaked for 1 hr., partially dried pieces for 2 hr. and the dry salted pieces for 3 hr., all in mechanical shaker. After soaking for the respective periods, the soak liquors were analysed for nitrogen and hydroxyproline. Data obtained in the case of partially dried and dry salted hide pieces are calculated on initial wet salted weight (39.2% moisture content) basis and presented in Table IV.

It may be observed that dehydration of the salted hide does not appreciably affect the hydroxyproline extraction (Table IV). When calculated on the initial wet salted weight, hydroxyproline extracted from a dry salted hide is only about 3% less than that from control (wet salted hide) whereas the extractable nitrogen is about 11.0% less in the case of dry salted hide. Period of soaking, however, is to be extended when dry salted hide is analysed for hydroxyproline.

3.1.5. Effect of different percentages of salt.

The claim that the hydroxyproline extraction method can be suitably applied in assessing the quality of hide was next examined. In the first instance, the minimum quanitity of salt required for primary salting was found out.

Samples were taken from freshly slaughtered cattle hide, freed from adhering fat and flesh and then salted with 10, 15, 20 and 25% salt on green weight. Salted hide pieces were taken separately in closed containers and stored at room temperature for two weeks. Observations were made on the quality of hide pieces which were then soaked for 1 hr. in a shaker. Nitrogen and hydroxyproline in soak liquor were determined. Results are presented in Table V.

It is evident from the results in Table V that a hide salted with 20% or more salt can be preserved well two weeks or more. Slight deterioration in hide quality has taken place within the period of observation when 15% salt is applied and considerable damage has been caused when it is salted with 10% salt.

3.1.6. Quality of wet salted hide during storage.

The quality of salted hide as affected after different storage periods was next studied by extractable hydroxyproline method. Fresh hide samples were salted with 40% salt and then stored at room temperature (about 30°C). Samples were taken every month, soaked and the nitrogen and hydroxyproline present in soak water were estimated as before. Results obtained are tabulated in Table VI.

It may be observed from Table VI that up to 2 months' storage at a temperature of about 30°C no hydroxyproline is extracted and after 3 months, hydroxyproline is found to be extracted in traces. Hydroxyproline content in soak liquor increases with further increase in storage period. Slight 'hair-slip' is also noted after 3 months' storage when traces of hydroxyproline are found present in soak liquor.

It may further be noted that development of 'red-heat' is not always directly responsible for the degradation of collagen as is evidenced from the absence of hydroxyproline in the soak liquor after the appearance of 'red-heat'.

TABLE V

Extractable hydroxyproline and nitrogen from hides salted with different percentages of salt during primary salting

Percent salt applied on green weight	Condition of salted hide (observations after two weeks storage)	Extractable hydroxyproline N	Extractable collagen N	Extractable N
		% of total N		
10	Easy hair-slip, putrid smell, moist, no salt is presented on the surface	0.009	0.11	3.51
15	Slight hair-slip, slight ammoniacal smell, moist, no salt is present on the surface	0.005	0.06	4.74
20	No hair-slip, smell not so fresh, moist, no salt is present on the surface	Trace	Trace	1.26
25	No hair-slip, fresh smell, some salt is present on the surface	Nil	Nil	1.14

TABLE VI

Extractable hydroxyproline and nitrogen of salted hides stored for different periods

Period of storage	Conditions of salted hide	Extractable hydroxyproline N	Extractable collagen N	Extractable N
		% of total N		
1 week	Good	Nil	Nil	0.56
1 month	'Red-heat' developed, otherwise good	Nil	Nil	0.80
2 months	'Red-heat' developed further, otherwise same as in 1 month	Nil	Nil	1.03
3 months	'Red-heat,' very slight hair-slip, smell not so fresh	Trace	Trace	1.09
4 months	Same as in 3 months but with more hair-slip	0.005	0.06	1.48

3.2. Discussion.

The present study reveals that good correlation exists between the extractable hydroxyproline and the quality of unsalted or salted hide. Extractable hydroxyproline is found to be absent or present in traces in hides staled upto 24 hrs. at a temper-ture of about 30°C under the existing conditions of experiment. It is thus evident that hide collagen remains practically unaffected up to 24 hrs. staling after which period collagen is readily attacked by micro-organisms. During the initial stages of staling the globular proteins may be preferably attacked but degradation of globular proteins to a greater extent takes place possibly after 24 hr. staling.

It has been observed that 'hair-slip' starts after 28-30 hrs. of staling at a temperature of about 30°C and becomes easy after staling for 40 hrs. In some cases grain damage has been found to occur to some extent after a 40 hr. staling. Thus it appears that collagen or leather making substance is not much affected till 'hair-slip' starts and an easy 'hair-slip' due to microbial action is found to be associated with loss of collagen.

It is, however, difficult to define categorically the limit of extractable hydroxyproline content that may be permitted in good quality hides but, on the basis of the present investigation, it may be said that the best quality hides should not permit any extractable hydroxyproline; hides having upto 0.005% extractable hydroxyproline nitrogen may be considered as fairly good and those containing more than 0.02% extractable hydroxyproline nitrogen as poor in quality.

Extractable nitrogen is found to vary from hide to hide and depends on other factors e.g., presence of blood and manure, type of cure, etc., and so cannot be considered as a criterion for quantitative determination of hide quality. Under the present experimental conditions, it appears that extractable nitrogen for a good quality cattle hide should not be more than 3%.

But this is much lower than that of the limit suggested by Whitmore et al [7] and may be due to the fact that hide pieces have been soaked in their experiment for a much longer period i.e. 24 hr.

To find out the extent of deterioration that has taken place in the hide before it is dry salted, estimation of extractable hydroxyproline may provide valuable information. While extracting the hydroxyproline of dry salted hide, the soaking period should, however, be extended to 3 hr. or more.

3.3. Recommended procedure.

A hide piece weighing about 50-100 g. is cut out, cleaned free of excess salt and surface blood, taken in a bottle with 5 times its weight of distilled water and shaken in a mechanical shaker for 1 hr. The soak liquor is then filtered and made up to 250 ml. in a volumetric flask. Hydroxyproline is then estimated and calculated as hydroxyproline nitrogen and expressed as per cent of total hide nitrogen which should not exceed 0.005% for a moderately good quality leather. This method is quite simple and will give a quantitative measure of the hide quality.

4. Inter-relationship of hide quality as estimated by extractable hydroxyproline nitrogen of soak water to the quality of finished upper leather.

In the previous study it was pointed out that a cattle hide having upto a maximum of 0.005% extractable hydroxyproline nitrogen (% of total N) might produce fairly good quality finished leather. In other words, fairly good leathers might be produced from hides which were staled for a period sufficient enough to show slight 'hair-slip'. But in order to prove the effectiveness of this method of quality assessment, experimental evidences are to be put forward and so the present work was undertaken to study the effect of staling on the quality of chrome tanned upper leather.

4.1. Experimental procedure and results.

Freshly slaughtered cattle hides (6 nos.) were collected from slaughter house and made into 12 sides by cutting along the line of backbone. The left hand sides were then salted with common salt in the usual way and were considered as control sides. The right hand sides were left for staling (temperature range 33-26°C) for a day till 'hair-slip' commenced. It was observed that 'hair-slip' took place in certain areas after about 23-24 hr. staling. The staled sides were then salted with salt as before. After piling for 3 days all the salted sides were kept in storage for a period of one month at room temperature (about 30°C).

Experimental samples were then taken from each of the control and experimental sides and extractable hydroxyproline nitrogen in each sample was estimated by the method mentioned in 3. The values obtained are presented in Table VII.

It appears from Table VII that traces of hydroxyproline nitrogen are present in soak water from fresh salted sides. But hydroxyproline nitrogen present in staled hides ranges from 0.002 - 0.004%. These values correspond quite well with the values of extractable hydroxyproline nitrogen obtained in the earlier study from hides where 'hair-slip' has just commenced.

All the sides were taken in a single lot and tanned and finished into full chrome shoe upper leather. Tannery yields during processing of the sides and area yield of leather are presented in Tables VIII and IX.

An analysis of the data in Table VIII shows that salted weight calculated as per cent on raw weight appears to be slightly higher in case of staled sides. As staled hides may retain more moisture and salt after wet salting[62] it seems possible to have such variation in salted weight. On the other hand, both soaked and limed weights (% on raw weight) are found to be somewhat less in staled hides. Leather yield (sq. ft./lb. of hide or pelt) calculated on raw and salted weight seems to be slightly less in staled hides but appears to be equal when calculated on soaked and limed weight (Table IX).

A comparative assessment of the quality of the leathers shows that there is no appreciable difference

Table VII

Extractable hydroxyproline (% of total N) present in soak liquors from fresh and staled hides

Sample No.	Fresh sides	Staled sides
1	Trace	0.004
2	Trace	0.004
3	Trace	0.003
4	Trace	0.004
5	Trace	0.002
6.	Nil	0.002

Table VIII

Tannery yields during processing of the fresh and staled sides

Tannery weights	Fresh sides		Staled sides	
	Wt.in lb.	% on raw wt.	wt.inlb.	% on raw wt.
Raw wt.	50.25	-	48.25	-
Salted wt.	41.25	81.70	40.50	83.94
Soaked wt.	48.75	97.02	45.0	93.26
Pelt wt.	43.5	86.59	40.25	83.42

Table IX

Area yield of leather obtained from fresh and staled sides

Quality of hide	Area in Sq.ft. per lb. of			
	Raw hide	Salted hide	Soaked hide	Limed pelt
Fresh sides	1.03	1.25	1.07	1.20
Staled sides	1.00	1.19	1.07	1.20

between the control and experimental leathers. Control leathers are slightly more full and firm and the experimental leathers are slightly more mellow and flat.

Physical properties e.g. tensile strength, elongation, stitch tear strength, tongue tear strength, grain cracking strength and bursting strength were determined and presented in Table X.

Data presented in Table X reveals that there is no significant variation in stitch tear strength, tongue tear strength, grain cracking and bursting strength of the leathers made from control and experimental sides. Per cent elongation may be slightly higher and the tensile strength in perpendicular direction appears to be slightly lower in leathers from staled hides.

4.2. <u>Discussion</u>.

Extractable hydroxyproline nitrogen present in the experimental staled sides lies within the limit of 0.005% which tends to indicate that these hides are capable of producing fairly good leathers. During processing the tannery yields and leather yield (area yield), all calculated on green weight, appear to be slightly less in staled sides than control sides. These slight variations in tannery yields and area yield are possibly indicative of the slight deterioration in the basic quality of the raw material although the qualities of the finished leathers may not be appreciably affected. In the present study only six sides have been taken for comparison and so greater emphasis cannot be laid on the slight variation in yield.

Visual inspection of the leathers reveals that there is no significant difference in the assortment of the experimental and control leathers. Average physical properties of the leathers also do not vary to any greater extent. The present investigation thus points out that a hide, if allowed to be staled for a period upto the beginning of 'hair-slip' and is not further deteriorated in quality during storage, may

Table X

Physical properties of the leathers made from fresh and staled side

Physical properties	Fresh		Staled	
		‖	⊥	‖
1. Tensile strength (lb/sq.inch				
Maximum	6404	5542	5026	5435
Minimum	3583	3242	3395	3248
Average	5194	4269	4321	4334
2. Elongation(%)				
Maximum	55	55	59	56
Minimum	38	39	40	44
Average	47	46	50	49
3. Stitch tear strength (lb/inch)				
Maximum	2045	1940	1835	1854
Minimum	1333	1316	1475	1339
Average	1689	1631	1638	1634
4. Tongue tear strength (lb/inch)				
Maximum	447	462	369	457
Minimum	330	300	120	254
Average	370	389	307	371
5. Grain cracking strength (lb/sq.inch/inch)				
Maximum		17549		19858
Minimum		5542		7068
Average		11234		11684
6. Bursting strength (lb/sq.inch/inch)				
Maximum		20320		19858
Minimum		10622		10380
Average		15483		14837

be affected in quality to a slight extent but the qualities of the finished leathers are fairly comparable to that of the leathers obtained from fresh salted hides.

5. <u>Summary and conclusion</u>.

1. A method has been worked out for the quantitative determination of the extent of deterioration in hide quality during staling or during long storage based on the estimation of extractable hyproxyproline present in soak water. Estimation of extractable hydroxyproline nitrogen (% of total N) was found to give a measure of the degradation of hide collagen or loss of leather making substance. Hides possessing extractable hydroxyproline nitrogen upto 0.005% are expected to produce fairly good leathers but having more than 0.02% extractable hydroxyproline nitrogen hides may produce poor quality leathers. The quality of dry salted hides and preserved untanned pelts may also be assessed by this method.

2. A pilot plant experiment was conducted to collect data in support of the above method of assessment of hide. Corresponding fresh and staled sides (till 'hair-slip' started) were stored for a period of one month after wet salting and were then evaluated for quality by extractable hydroxyproline method. The sides were then tanned and finished into full chrome shoe upper leathers. The interpretation of the quality index data for staled sides and the qualities of the finished leathers produced from them corresponded favourably well. Leathers produced from staled sides were fairly good in comparison to the leathers from control fresh sides.

CHAPTER II

1. Interfibrillary materials in cattle hide and their influence on processing and on properties of finished leather

2. Methods

2.1. Protein constituents in hide

Tancous[16] presented informative data about the non fibrous protein components in hide but objections may be raised[63] about the procedure followed by her to estimate the globular proteins. Debeukelaer and Marbach[64] followed a procedure in which the hide was first extracted with 10% NaCl to remove the globular proteins followed by extraction with half saturated lime to eliminate the lime soluble proteins. The residual material was then treated with 0.1% HCl at 85°C for two hours. Keratin and elastin were removed as residuep collagen was estimated from the filtrate by direct Kjeldahl estimation. Thabraj et al[17] followed a procedure where albumin, globulin, mucoid and collagen of goat skin were estimated. In their study the value for collagen was obtained by converting hydroxyproline data.

In the present investigation, Debeukelaer and Marbach's method was followed upto the extraction of lime soluble mucoid material and then hydroxyproline estimated by the Neuman and Logan method[60] and converted into collagen.

Hide was dehaired by first clipping the hair and then shaving it off. Excess fat and flesh were removed by careful fleshing. The hide piece was then chopped into small pieces and minced in a hand operated mincing machine in the presence of ice. About 10 g. minced material was used for extraction. The minced material was taken in a shaking bottle and extracted with 10% salt solution (hide: salt solution: 1:10) for one hour in a mechanical shaker. This was then centrifuged at 2000 r.p.m. for 15 mt. and the supernatant was decanted off through glass wool. Extraction was repeated twice with a fresh quantity of 10% salt solution using 1 part of merthiolate per 10,000 parts of solution as an antiseptic during the extraction. The residue was washed twice with 10% salt solution and the filtrate and washings were combined and made up to a required volume. The filtrate contained globular proteins and non-protein nitrogen (A). An aliquot of the filtrate was analysed for nitrogen by Kjeldahl method. Trichloroacetic acid was added to another aliquot of the filtrate to give a final concentration of 4% of the acid[65] and the coagulable proteins were coagulated by heating over a water bath. This was filtered and the filtrate was analysed for nitrogen by the kjeldahl method which gave the value for non-protein nitrogen (B). Globular protein was calculated from the difference of A and B.

The residue after the extraction of globular proteins was extracted with half saturated lime (1:10) for one hour and centrifuged at 2000 r.p.m. for 15 mt. The supernatant was decanted through glass wool. Two more extractions with fresh quantity of half-saturated lime were carried out. The residue was washed with half-saturated lime and the filtrate together with the washings was collected and made up to a known volume. An aliquot was taken for nitrogen estimation (Kjeldahl method) and this gave the value for lime soluble protein nitrogen.

The residue was washed well with distilled water, dried in a basin to constant weight and powdered. A portion of it was digested with 6N HCl for 18 hr. at 105°C in a sealed tube and the hydrolysate was made up to a known volume. Percentage of collagen was calculated by estimating hydroxyproline by the Neuman and Logan method using the conversion factor 7.52[9] (a separate moisture estimation was made). The hydroxyproline method was preferred as it gave a more direct measure of collagen than the kjeldahl method. The remaining protein constituents are termed as unextractable non-collagenous protein which may include keratin, elastin and unextractable interfibrillary proteins.

Kjeldahl analysis was always done in duplicate. 4% boric acid and 0.01N HCl were used to trap and titrate the ammonia released.

2.2 Estimation of hexosamine

Hexosamine was estimated according to the method of Elson and Morgan as adopted by Windrum, Kent and Eastoe[66] with slight change. 1 ml. of the test sample was treated with 2 ml. acetyl acetone (1.5 ml acetyl acetone made up to 50 ml with 2.5N Na_2CO_3). This was heated for one hour in a water bath at 95°C and allowed to be cooled and 10 ml. of 95% ethanol and 1 ml. of Ehrlich's reagent (1.6 gm p-dimethyl amino benzaldehyde in 30 ml. conc. HCl and 30 ml. ethanol) were added. After standing for one hour, the intensity of the red colour developed was measured by a D.U. spectrophotometer at 530 mμ.

2.3 Estimation of uronic acid

Uronic acid was estimated according to the method of Bitter and Muir[67]. 5 ml. of H_2SO_4 reagent was taken in tubes and cooled to 4°C; 1 ml of sample was carefully layered on to the acid. The tubes were shaken gently and then they were heated for 10 mt. in a vigorously boiling distilled water bath and cooled to room temperature. 0.2 ml. carbazole reagent (0.125% in absolute alcohol) was then added to the tubes. The tubes were shaken again, heated in the water bath for a further period of 15 mt. and cooled to room temperature. The optical density was then read at 530 mμ.

2.4 Estimation of tyrosine

Colorimetric assay method of Cobbet, Kensington and Ward[68] was followed in estimating tyrosine.

2.5 Estimation of Hexose

Hexose was estimated by phenol sulphuric acid method as suggested by Dubois et al[69].

2.6. Estimation of hydroxyproline

Stegemann's method was followed in estimating hydroxyproline (if not otherwise mentioned) as simplified by Bergman and Loxley[70].

3.0 Influence of green salting and pretanning operations on the removal of interfibrillary proteins of cattle hide

3.1 Experimental procedure and results

3.1.1 Locational variations of the interfibrillary proteins

Freshly slaughtered hide was green fleshed and samples were cut from the right hand side in different locations (Fig.4) and kept in polyethylene bags in a freezing box at 0°C till they were analysed. The left side was then cured by wet salting and stored for a period of 3 weeks. Samples were then cut from different sites of the salted side identical with those of the fresh samples (1A,2A,3A,4A, and 5A). The samples were washed in water to remove excess salt and then analysed for different protein constituents.

The left side was then soaked in water for a period of six hours and limed for 40 hr. in a liquor comprising 2.5% Na_2S, 0.5% ammonium sulphate, 8% lime and 350% water. The side was then unhaired, fleshed, washed well and delimed with 1% ammonium sulphate and 150% water for about an hour. The side was bated with 0.5% C.L.R.I. bate (No.2) for 30 mt. scudded and then washed. Pickling was done with 1.25% H_2SO_4, 5% salt and 80% water. Samples were then cut from different positions (1B, 2B, 3B, 4B and 5B). These samples were kept at 0° for a few days till they were taken for analysis.

Results obtained are given in Table XI

3.1.2 Effect of various treatments of the hide

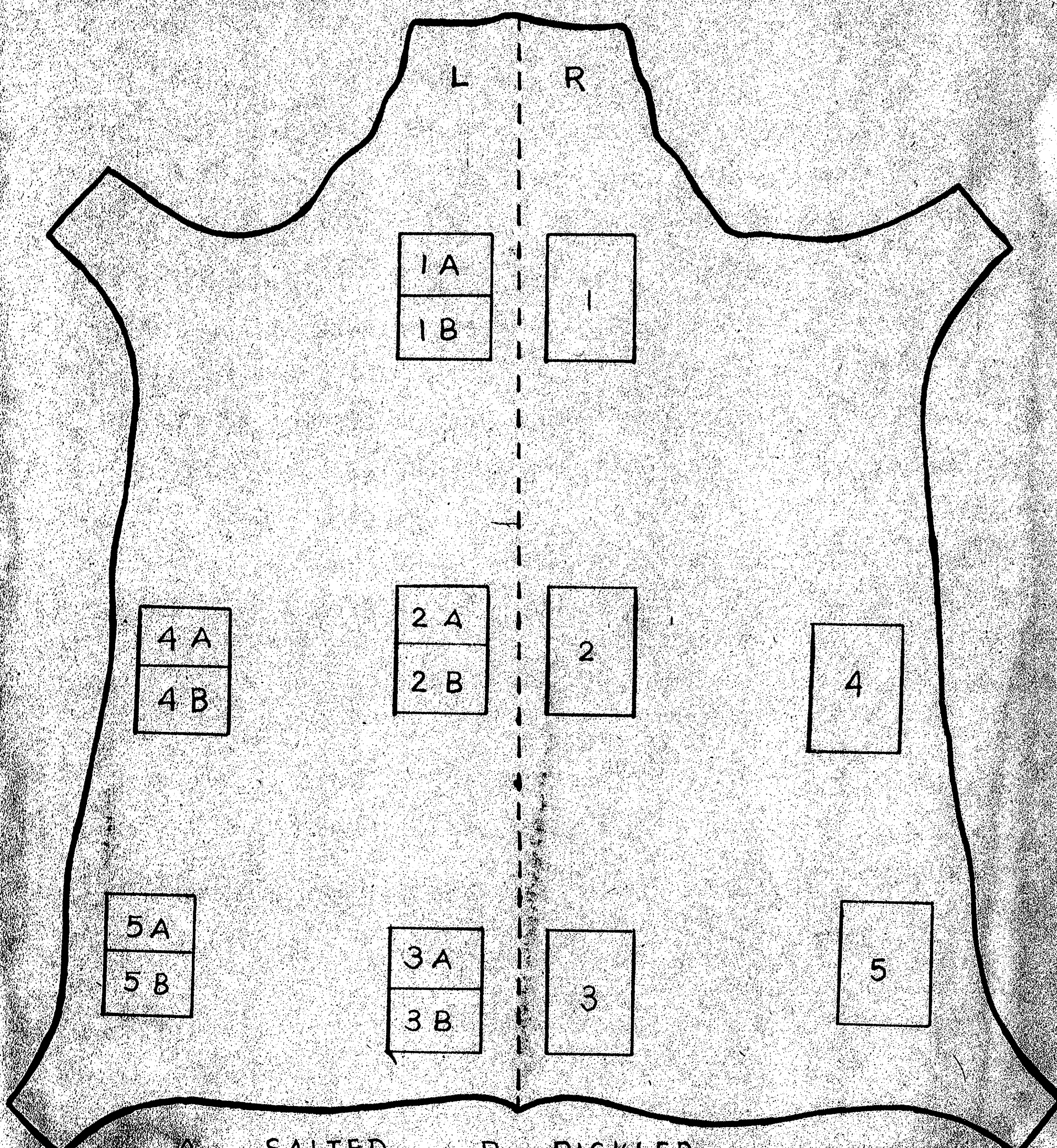
Hide pieces were treated in different ways as mentioned below:

(i) Raw hide: Fresh raw hide sample was kept at 0°C in a polyethylene bag for about an week before experiment.

(ii) Air dried: Hide piece was dried in the laboratory at room temperature (about 30°C)

(iii) Dry salted: Hide piece was cured with 35% salt and then dried at room temperature

FIG.-4



A - SALTED AND WASHED B - PICKLED

Table XI

Different protein constituents in hide after wet salting and pretanning operations*

Pre-tanning operations	Location	Salt soluble protein nitrogen (% of total N)	Nonprotein Nitrogen (% of total N)	Lime soluble nitrogen (% of total N)	Collagen Nitrogen (% of total N)	Unextractable non-collagenous nitrogen (% of total N)
Fresh hide	A	4.5	2.2	2.6	71.3	19.4
	B	3.4	2.2	1.9	72.6	19.9
	C	2.1	1.6	1.7	76.0	18.6
	D	2.8	2.1	2.4	72.0	20.7
	E	2.9	2.3	2.2	71.5	21.1
	Average	3.14	2.08	2.16	72.68	19.94
Salted hide	A	2.5	2.0	2.2	73.2	20.1
	B	1.9	1.8	1.7	75.0	19.6
	C	1.0	1.4	1.6	77.4	17.6
	D	2.0	1.5	2.1	74.5	19.7
	E	2.2	1.8	1.9	73.5	20.6
	Average	1.92	1.7	1.9	74.7	19.96
Pickled pelt	A	0.06	1.2	0.84	86.8	11.10
	B	0.07	1.1	0.87	87.8	10.16
	C	0.04	0.89	0.63	89.0	9.44
	D	0.04	0.87	0.71	87.4	10.98
	E	0.05	1.10	0.79	86.20	11.86
	Average	0.52	1.03	0.77	87.44	10.71

* Data presented in the above table are the average values of samples from two hides

(iv) Extracted with 10% salt: The hide piece was extracted twice with 10% salt solution and then cured with salt as usual.

(v) Extracted with 10% salt and half saturated lime: The hide piece was first extracted thrice with 10% salt solution and thrice again with half saturated lime solution and then cured with salt.

(Vi, vii and viii) These samples were applied with salt and stored in wet salted condition.

3.1.2.1 Processing of the hide samples

Fresh hide piece was soaked in water for a couple of hours. Liming, deliming, bating and pickling were done in a similar way as in the previous experiment. Dried hide was soaked in water for 3 days and the dry salted hide for 2 days in the presence of an antiseptic. The following procedures upto pickling were the same as above.

The sample extracted with salt solution prior to salting was soaked in water for about 4 hr. and processed as above. The sample extracted with 10% salt and half saturated lime prior to curing was also processed as above. Samples Vi, vii and viii were soaked in water for about 6 hr. and then limed in different ways. Standard quality upper leathers could be produced by adopting any of the following liming processes.

(vi) Short liming: Soaked hide piece was taken in lime liquor of the following composition. 4% Na_2S, 6% $Ca(OH)_2$, 3% hypo and 150% water. The hide piece was treated in the above lime liquor by drumming for a period of 6 hr., the drum being run for 10 mt. every hour.

(vii) Painting: Soaked hide piece was painted on the flesh side with a paste of 2.5% Na_2S, 12% $Ca(OH)_2$ and 20 parts water and left overnight. The next morning the hide was unhaired and then put in a liquor containing 1.5% Na_2S and 300% water with occasional handling. Next day, the hide piece was taken out, fleshed, washed and then delimed.

(viii) Pit liming: Soaked hide piece was limed in a liquor comprising 1.5% Na_2S, 5% $Ca(OH)_2$ and 300% water for 72 hr. with occasional handling each day.

TABLE XII

Different protein constituents in hides treated in different ways after pretanning operations.

Hides treated in different ways	Salt soluble protein N	Non-protein N	Lime soluble protein N	Collagen N	Unextractable non-collagenous protein N
Raw hide	0.06	1.56	0.95	85.10	12.33
Air dried	0.20	2.14	0.85	82.40	14.41
Dry salted	0.10	1.26	0.71	84.00	13.93
Salt extracted	0.04	1.21	0.74	86.80	11.21
Salt + lime extracted	0.04	1.30	0.64	86.10	11.92
Short liming	0.04	1.45	0.90	85.80	11.81
Normal liming	0.06	0.96	0.80	86.50	11.68
Long liming	0.05	1.25	0.59	88.00	10.11

After usual deliming, bating and pickling all the samples were analysed for their protein constituents and the results obtained are presented in Table XII.

3.2 Discussion

It appears from Table XI that the protein constituents in different locations of a fresh raw hide may differ to a certain extent. The amount of globular (salt soluble) protein nitrogen is found to be maximum in the neck area (position 1) and is gradually reduced towards the butt area (position 3) where it is minimum. The amount of globular proteins in the belly (position 4) and shank (position 5) areas is in between the values for the neck and butt areas. Variation in lime soluble protein in different areas of the hide is however small, but the maximum amount of lime soluble protein nitrogen is also found in the neck area and the minimum in the butt area. Tancous noted a reduction in the amount of globular proteins from neck to butt area in calf skin[16] and steer hide[71]. Globular protein nitrogen and lime soluble protein nitrogen was found to vary[72] with age and in different locations of skins.

According to Rosenthal[73] calf skin contained about 4.5% coaguable nitrogen and 2.8% mucoid. Debeukelaer and Marbach[64] reported 2.8% salt soluble globular proteins and 1.0% lime soluble protein in fresh steer hide. Following a similar extraction method, 4.9% globular proteins and 5.7% mucoid (on dry goat skin) were found in fresh goat skin[17]. In the present study, the average values for salt soluble proteins and lime soluble proteins are 3.14% and 2.16% respectively. It is, however, recognised that calf and goat skins may have more interfibrillary proteins than aged cattle hide.

Non protein nitrogen does not vary much with location on the hide except that it is minimum in the butt area. Collagen nitrogen on the other hand is found to be maximum in the butt area and minimum in the neck area. Tancous reported 73.1% collagen nitrogen (by Kjeldahl estimation) in calf skin[16] and 86.3% collagen nitrogen in steer hide[71]. According to Debeukelaer and Marbach[64] collagen nitrogen in steer hide was 89.6%. Following the hydroxyproline method, 77.5% collagen (on dry goat skin) was found by Thabraj et al[17] in goat skin. In the present investigation, the average collagen content of cattle hide appears to be 72.7%. Unextractable non collagenous protein nitrogen in fresh hide is found to vary slightly within the range 18.5 to 21.0%.

After green salting and washing of the hide, a considerable proportion of globular proteins is found to be extracted and removed. Non protein nitrogen and lime soluble proteins are also removed to some extent. The amount of collagen nitrogen, however, appears to be slightly increased, but this is a consequence of the removal of non-collagen nitrogen and the fact that the removal is expressed as percentage of the total nitrogen. Removal of globular proteins and lime soluble proteins to different extents[16,17,71] and the slight increase in collagen content[16,64,71] after salt curing and soaking were also reported by other investigators. Okamura and Kawamura[72] however, observed no essential difference in collagen content between green and salted hides. It may further be noted that unextractable non-collagenous protein nitrogen remains unaffected by wet salting and washing. The trend in areawise variation of different protein constituents of the hide after salting and washing is somewhat similar to that of fresh hide.

After pretanning operations i.e. after pickling, extractable globular proteins are found to be mostly removed (98%) from the hide. Lime soluble proteins and non-protein nitrogen are found to be removed after pickling to the extent of 64% and 50% respectively. Collagen nitrogen is found to be increased by about 20% on the collagen content present in fresh hide but the amount of collagen nitrogen in pickled pelt appears to be slightly low. Thabraj et al[17] reported the removal of about 80% globular proteins and 59% lime soluble protein from goat skin after pretanning operations. According to Tancous[16], 89% globular proteins (including mucoids) were removed from calf skin after pickling. An increase in collagen nitrogen by 29% was noted by her. In the present study the amount of unextractable non-collagenous protein is found to be appreciably reduced (46%) in pickled pelt. Although it is quite possible to have certain differences regarding the extent of removal of different interfibrillary proteins depending on the type of hide or skin, their initial protein constituents, processing operations and the existing temperature, it is apparent from the present data that the extractable globular proteins are removed to a great extent after pretanning operations but about 35% lime soluble proteins remain in the pelt that is ready for tanning.

In order to produce pelts having varying amounts of interfibrillary proteins, hide samples were treated in different ways so that some of them e.g. raw, air dried and dry salted samples might retain more and others might have less amount of interfibrillary proteins than a normal wet salted hide. After soaking, the samples were put through the same pretanning operations. The wet salted samples that were limed in different ways were also delimed, bated and pickled along with other samples. Data presented in Table XII indicate that irrespective of the removal of interfibrillary proteins to varying extents in precuring stage, practically the same small amount of globular proteins is present in all samples except in the air dried and dry salted ones where the values are slightly higher. It is possible that the interfibrillary proteins present in these samples got partially denatured due to drying thus affecting the removal of the soluble proteins. Lime soluble proteins present in the pelts vary within a small range although it appears that the removal is slightly more in the case of the samples initially extracted with 10% salt solution and half saturated lime and also in the other case, where the sample was subjected to long liming. Collagen nitrogen appears to be slightly less in air dried sample but slightly more in the sample subjected to long liming. On the other hand, unextractable non-collagenous protein nitrogen is found to be slightly higher in air dried sample and slightly lower in case of the sample subjected to long liming.

The results of the present investigation thus point out that wet salted hide, after normal pretanning operations, retains small amounts of extractable globular proteins which may be considered to have little effect on the properties of finished leathers. A considerable proportion of lime soluble protein is, however, retained by the hide after pretanning processes which may influence leather quality but this requires further confirmation. But it is felt that any drastic treatment to remove further amounts of lime soluble proteins may probably act also on collagen in some way thus impairing leather quality irrespective of the quantity of the non-fibrous proteins left in the pelt. The effect of the presence of unextractable non-collagenous proteins has not been considered in the present study.

4. Studies on certain non-protein components of interfibrillary materials extracted from cattle hide

4.1 Experimental procedure and results

A freshly slaughtered cattle hide was collected from the slaughter house, washed, green fleshed and hide pieces were cut and unhaired with the help of a safety razor. They were then minced by a mincing machine as before (2.1 - Ch.II). Minced hide homogenates were extracted with 10% sodium chloride solution and then extracted with a half saturated calcium hydroxide solution in the same way as in 2.1. The filtrate of half saturated lime extraction was divided into two portions. The first portion was analysed as it is but the second portion was acidified with acetic acid to pH 4 when the mucoid materials were precipitated. The precipitate was recovered by centrifuging, washed well and dried in a vacuum desiccator.

The residue after lime extraction was then taken in 0.1 molar acetic acid and autoclaved at 15 lbs. pressure for 9 hours, filtered and the filtrate was precipitated with trichloroacetic acid to 5% concentration.

All the filtrates were dialysed against distilled water, concentrated to dryness and analysed for the various parameters i.e. hexose, uronic acid, hexosamine, tyrosine and hydroxyproline. The results obtained are expressed as micrograms per gm. of moisture free hide, and are presented in Table XIII.

In order to find out the effect of solvent treatment and removal of lipids on the extraction of interfibrillary materials, 200 gm. of minced hide were extracted thrice with fresh quantity of the solvent mixture (Acetone:petroleum ether:methanol = 1:1:1) and then with chloroform to remowe the fatty materials. The residue was then extracted with sodium chloride and half saturated lime solution and the extracts were analysed as mentioned earlier. Data obtained are presented in Table XIII.

4.2 Discussion

In the previous work (3 - Ch.II) hide tissue homogenates were extracted with sodium chloride and half saturated lime solution and analysed for different protein constituents of extractable interfibrillary materials. In the present study a preliminary investigation was made on some of the non protein constituents of the extractable interfibrillary materials present in cattle hide either in a loosely or firmly bound condition. The presence of tyrosine and hydroxyproline in the extracts was also examined.

It appears from the data (Table XIII) that the major portion of non protein constituents and non fibrous proteins of the extractable interfibrillary materials are extracted by salt solution. Sodium chloride extract is mainly composed of hexose which is followed by tyrosine, uronic acid and hexosamine are also present to certain extents. The ratio of uronic acid and hexosamine appears to be roughly 1:1. It may be noted that about 77% of the hexose, 84.5% of uronic acid, 80% of hexosamine and about 90.5% of tyrosine are extracted by sodium chloride solution. Although presence of hydroxyproline in sodium chloride extract was reported by Adelmann et al[74] it is found to be absent or present only in traces in the present study. The absence of salt soluble collagen may be due to the fact that the hide was obtained from an old

TABLE XIII

Different constituents of interfibrillary materials in cattle hide

Different constituents	NaCl (10%) extract	Lime (half saturated) extract	Lime extract precipitated at pH4 with acetic acid	Autoclaved, centrifused, decanted and precipitated with TCA. (5% concentration)	NaCl (10%) extract of solvent treated hide
Hexose	932.0	228.0	157.6	53.2	416.0
Uronic acid	168.0	22.6	20.4	8.3	160.0
Hexosamine	185.0	30.5	21.4	15.0	143.8
Tyrosine	446.0	36.3	-	10.6	-
Hydroxyproline	-	-	-	2.2	-

animal and the content of neutral salt soluble collagen in hide depends on the age of the animal[75].

The principal constituent of the lime extract also appears to be hexose although much less in quantity than present in salt extract (18.79%). Other constituents of lime extract are uronic acid (11.34%), hexosamine (13.23%) and tyrosine (7.36%). The presence of tyrosine in lime extract indicates that some of the globular proteins that are not extracted by salt are extracted with half saturated lime.

After removal of the globular proteins from the hide, the mucoids may be precipitated on acidifying the half saturated lime extract with acetic acid[76]. Hexose, uronic acid and hexosamine are found present in this fraction but slightly less in quantity than in the alkaline fraction. This shows that lime extract contains other carbohydrate constituents besides mucoids.

Extraction of hide with 10% sodium chloride solution followed by half-saturated lime are capable of removing non-fibrous components of the hide that are loosely attached to collagen. To extract the firmly bound components, the remnants, after extraction with sodium chloride and half saturated lime, were subjected to autoclaving and the interfibrillary materials were precipitated with trichloroacetic acid. All the different components isolated in the earlier fractions are found present in this fraction also but only in small quantities. Hydroxyproline is found present in this fraction in small quantity. The present data thus reveals that the globular proteins and the carbohydrate constituents of the interfibrillary materials that are firmly bound with collagen are not extractable by normal pretanning operations.

Extraction of different components by 10% sodium chloride solution is found to be affected when the hide is treated and defatted by solvents. Hexose, uronic acid and hexosamine are found to be extracted. The amount of hexose extracted is reduced appreciably to about half the quantity of the fresh untreated hide. Tyrosine and hydroxyproline are found absent in this extract. It is possible that solvent treatment may have denatured the globular proteins thus inhibiting the extraction of interfibrillary proteins. This observation is in agreement with that of Pearson[77].

In the previous study (3 - Ch.II) it has been observed that about 98% of the globular protein nitrogen are extracted during pretanning operations. In the present study tyrosine is found to be extracted roughly to the same extent by sodium chloride and half saturated lime extraction. But more precise information about the non fibrous proteins and the carbohydrate constituents of the interfibrillary materials that are retained by the pelt after normal pretanning operation is yet to be obtained to elucidate the role played by them on the properties of finished leather.

5. <u>Summary and conclusion</u>

1. Different protein constituents in fresh cattle hide and in hides subjected to some of the beam-house operations were determined. Areawise variation in the protein constituents was studied in five different locations on a side. Salt soluble proteins (10% NaCl) and lime soluble proteins (one-half saturated lime) were found to be present to the maximum extent in the neck region and to the minimum extent in the butt area. Extractable salt soluble coagulable proteins were removed partially after green salting and subsequent washing of the hide and were almost completely removed after pretanning operations. About 35% of extractable lime soluble protein initially present in fresh hide was retained by pickled pelt and this unextractable lime soluble fraction may possibly have certain influence, if any, on the properties of finished chrome leather.

Determination of protein constituents in different pickled pelts obtained from hide samples treated in different ways indicated that removal of globular protein was comparatively less in air dried hide than in wet salted hide. In spite of different initial treatments, the protein constituents in the pelt samples varied only within a narrow range.

2. The interfibrillary materials in cattle hide extractable by sodium chloride solution (10%) and by half saturated lime solution were analysed for the non protein constituents like hexose, uronic acid and hexosamine and for amino acids e.g. tyrosine and hydroxyproline. It appeared that extractable non protein constituents and tyrosine were mostly extracted by salt extraction (about 77-90%) and by lime extraction (about 7 - 19%). Hydroxyproline was found to be absent (or present in traces) in these extracts. A small proportion of these components (about 2 - 6.5%) were present in hide firmly attached with collagen and were not extracted by normal extraction processes. Solvent treatment of the hide affected the extraction of interfibrillary proteins by sodium chloride solution.

CHAPTER III

1. Inter-relation of hide quality to the rate of tanning, leather yield and properties of finished leather.

2. Methods.

2.1. Assessment of hide quality.

Hide quality was determined by estimating the extractable hydroxyproline nitrogen as described earlier.

Chrome tanning process: Chrome tanning was done in the same way as reported in 2.5. Ch.-1.

2.2. Rate of chrome tanning.

Naidus and Browne[78] were of opinion that chrome tanning involves two distinct mechanisms (i) formation of cross links and (ii) non specific binding. It is well recognised that during chrome tannage crosslinking takes place by the co-ordination of chromium to the carbonyl group of collagen resulting in an increase in shrinkage temperature. The determination of Ts at different stages of tanning may thus represent the rate of tanning in respect to chemical characteristics of tanned collagen.

About 1% Cr_2O_3, although found sufficient to increase Ts to the maximum level, was not enough to impart other tanning characteristics of practical value e.g. fullness and suppleness of the leather . Fixation of Cr_2O_3 during tannage was thus considered to be the other criteria to determine the rate of chrome tanning.

2.3. Determination of Ts.

Samples were washed in water for 5 mt. and then Ts (°C) was determined in a Theis shrinkage meter using a glycerine bath. In case of vegetable tanned leathers Ts was determined in a Leather Shrinkage Tester (Model 16A,Engineering Specialities) using a water bath.

2.4. Fixation of Cr_2O_3.

Tanned samples were removed at different hours of tanning, washed for 3 hr. with 4 changes of water which was adjusted to the pH of the chrome liquor. The tanned pieces were then dried at room temperature and Cr_2O_3 fixed to the pelt was estimated by perchloric acid method.

2.5. Vegetable tanning process.

Different tanning procedures were followed by different investigators to study the rate of tanning. In many occasions tanning was done in tan liquors whose concentrations were maintained at the same level throughout the tanning operation. But in practice a weak liquor is used for early tannage and the strength of the liquor is gradually increased till the tanning is completed. Moreover, the composition of the tan liquor may appreciably change if the same liquor is used for tanning either alone or being strengthened by addition of fresh tannin. Leather yield and certain properties of the leathers are also to be examined. Considering the above points the procedure for tanning to be followed in the present study was adjusted as follows: salted buffalo hide samples were washed well and then soaked overnight in water. They were then limed in a liquor containing sodium sulphide 0.25%, lime 6%, old lime liquor 150% and water 150% with proper handling. After 4 days they were unhaired and then relimed for 3 days with lime 10% and water 300%. after liming they were fleshed, washed, delimed completely with ammonium sulphate (1%) and then put to a 10° Bk liquor made up of mimosa spray dried extract. Pelts were handled twice daily. Next day the strength of the liquor was adjusted to the original Bk. strength by adding a fresh quantity of extract powder. After two days the pelts were transferred to a 20° Bk liquor freshly prepared with extract powder. The pelts were handled as before and the strength of the liquor was readjusted on the next day. After two days' treatment the pelts were transferred to a new liquor of 30° Bk. In a similar way, pelts were treated for two days with each liquor of 40,60, 80 and 100° Bk. Tanning was done in glass jars at room temperature (30°C ± 2°) at the normal pH of the tan liquors. Tanned pelts were treated for another two days at 100° Bk. and then washed well and bleached, loaded, oiled, well set and then dried.

The leathers were finished as usual after rolling.

2.6. Rate of vegetable tanning.

It is recognised that vegetable tannage involves both (i) chemical crosslinking of polyphenolic OH groups of the tannins with the-CO-NH-group of peptide linkage through hydrogen bonding and thus raising the Ts and (ii) fixation and physical deposition of tannin without affecting the Ts but increasing the fixed tan. The increase in Ts during tannage was considered to be a criterion of tannage[79] and may be attributed to crosslinking during early stages of tanning. It had also been recognized that the amount of tannin fixed by the pelt at any time in the course of tanning would give further information about the extent of tanning. Mezey[36] estimated the rate of diffusion of tannin by staining histological sections at regular intervals and measuring the depth of penetration under the microscope. This method gives an indication of the extent of tanning during early stages i.e. till the pelt is struck through. Holmes and Wollenberg [47] recommended a method for the estimation of rate of tanning by measuring the weight gained by the pelt in the liquor during tanning till the equilibrium was reached.

First three methods were examined for their suitability in standardising a method or methods to study the rate of tanning. Because of appreciable difference in tanning procedure the last method was considered unsuitable for the present study. A preliminary investigation revealed that an estimation of Ts and fixed tan at regular intervals during tanning provided adequate information about the rate of tanning under the present experimental conditions. The extent of tannin penetration as determined histologically was found to be related to the rise in Ts and the maximum Ts was reached when the pelt was just struck through.

2.7. Fixed tan.

This was estimated in an indirect way. Samples were cut at regular intervals and were dried in the laboratory and then made into small pieces (5mm sq.).

They were taken in shaking bottles, distilled water was added to the bottles in the proportion of 1:5 (W/V) and then shaken in a mechanical shaker for 2 hr. to remove the water solubles.

The leather pieces were then dried at room temperature, made moisture free by drying at 105° C for 6 hr. and hide substance was then determined by kjeldahl method. The leather pieces being free from moisture and water solubles and considering the fat and ash content to be roughly constant, fixed tan may be determined as follows: 100 - Hide substance = Fixed tan. In order to find out the rate of increase in fixed tan on comparative basis, values for fixed tan obtained by the above method, may be considered acceptable.

2.8. Thickness of the pelt.

Thickness of delimed pelt was measured by a thickness gauge and expressed in mm.

2.9. Measurement of area.

Area of delimed pelt and leather was measured with the help of a planimeter. The area was first drawn on paper and then measured. Area yield of leather has been expressed as per cent increase in area on initial delimed area.

2.10. Pysical properties.

Tensile strength, tongue tear test and stitch tear strength were determined for chrome upper leathers in the same way as mentioned in Chapter I. For vegetable tanned sole leathers, water absorption was measured by the Kubelka method; apparent density was determined by mercury displacement method and abrasion was measured by an abrasion tester (American Instrument Co. Silver Spring, U.S.A.) after 400 revolutions. Tensile strength was determined as usual by an Avery tester (Type 6101).

2.11. Chemical composition.

Moisture, fat, Cr_2O_3 and hide substance were determined for upper leathers and moisture, fat, water solubles, hide substance and degree of tannage were determined for sole leathers according to the standard methods.

3. Effect of locational variation in cattle hide on processing and properties of chrome tanned upper leather.

3.1. Experimental procedure and results.

A wet salted cow hide was processed into full chrome upper leather according to the standard procedure. Samples were cut from different positions, e.g., butt, shank, belly and neck areas of the hide according to fig. 5 after soaking, liming, deliming and during and after tanning and Ts was determined. The results obtained are given in Table XIV.

In the above process for chrome tanning the extent of deliming was not the same in different areas of the hide. The butt area was found to retain more lime which will consequently affect the pH of tanning and hence chrome fixation. In order to avoid the non-uniform deliming one hide was delimed in the usual way and samples were then cut from butt, shank, belly and neck areas. Belly, shank and neck positions showed a very faint streak of lime at the centre but the butt position showed a good amount of lime in the central layer when tested with phenolpthalein. The samples from butt position were hence delimed further till the extent of deliming was the same in different positions and were then tanned in the laboratory in a 33% basic chrome liquor prepared out of 20% B & C chrome extract powder. The pelts were handled for 10 mt. every hour. The Ts of the tanned pelts were determined at different intervals of time. Fixation of Cr_2O_3 was also determined after different periods of tanning. Results obtained are given in Tables XV and XVI.

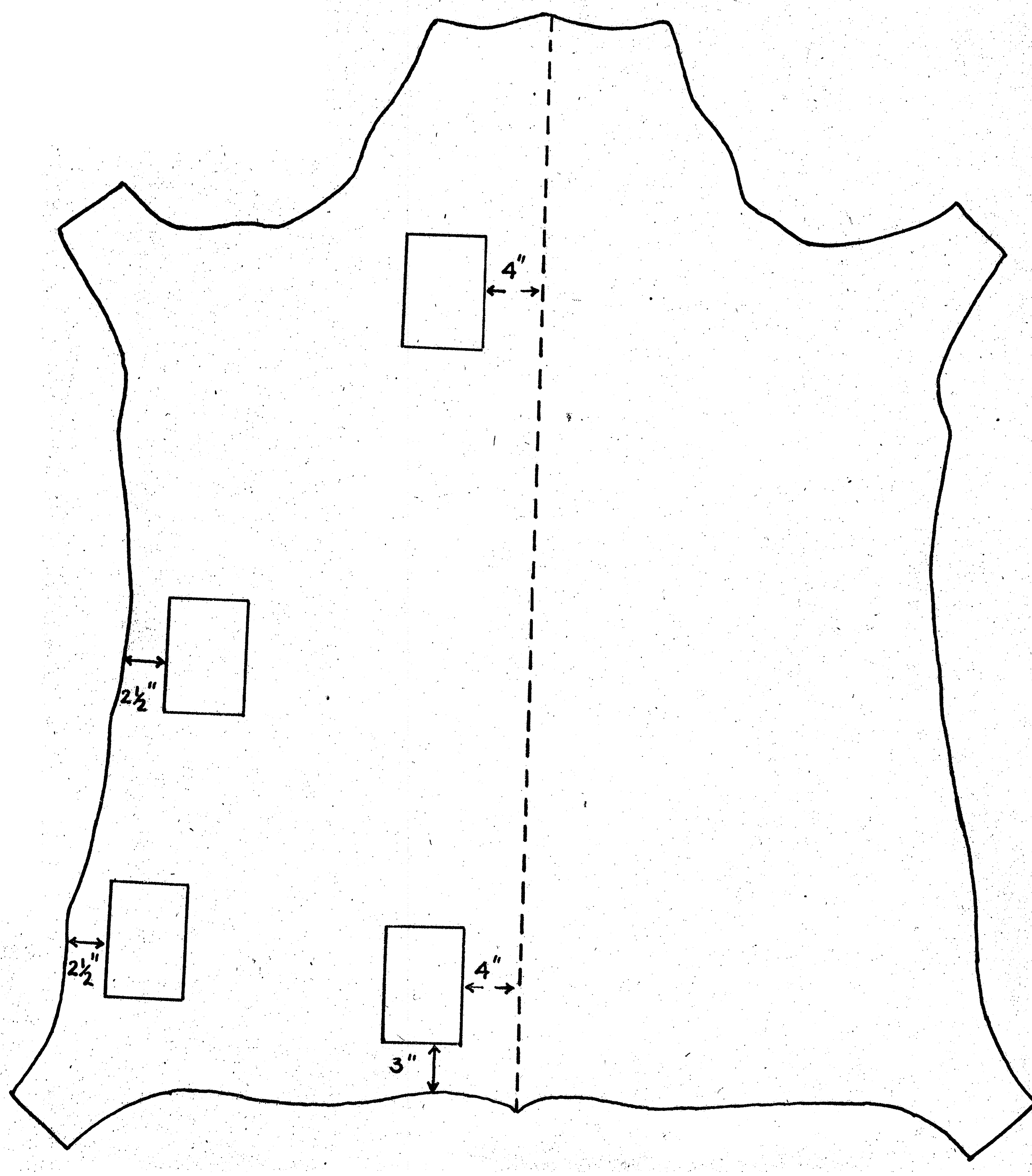
Effect of lime splitting:

Three sets of experiments were conducted to verify the effect of lime splitting on the quality of leather. In each experiment, 6 wet salted cow hides were taken. The left hand sides were split and shaved after tanning and were considered as the control lots. Right hand

Table XIV

Ts in °C of different areas of hide during normal processing

Area of hide	Thickness in mm.	Salted hide	Soaked hide	Limed for 20 hrs.	Limed for 42 hrs.	Delimed pelt	Tanned for ½ hr.	Tanned for 1 hr.	Tanned for 3 hrs.	Basified	Rechromed
Butt	2.7	72.5	70.5	59.0	57.0	66.0	86.5	95.0	100.0	104.0	116.0
Shank	1.4	72.0	70.0	54.0	54.0	66.5	85.0	90.0	97.0	103.0	116.0
Belly	1.7	71.5	70.5	56.0	56.0	65.0	82.5	92.5	96.5	106.5	117.0
Neck	2.3	72.0	70.5	55.0	54.0	66.0	83.0	91.0	98.0	105.0	114.0



4"
2½"
2½"
4"
3"

Table XV

Effect of uniform deliming on the Ts in °C of different areas of hide during tanning

Area of hide	Delimed pelt	Tanned for ½ hr.	Tanned for 1½ hrs.	Tanned for 3 hrs	Tanned for 5 hrs	Tanned for 24 hrs.
Butt	60.0	72.0	81.0	90.0	95.0	109.0
Shank	58.0	72.0	79.0	95.0	100.0	111.0
Belly	56.0	75.0	90.0	100.0	103.0	113.0
Neck	57.5	71.0	84.0	95.0	99.0	110.0

Table XVI

Fixation of Cr_2O_3 after different periods of tanning (% Cr_2O_3 fixed on dry weight basis)

Area of hide	Tanning time				
	½ hr.	1½ hrs.	3 hrs.	5 hrs.	24 hrs
Butt	0.929	1.337	2.138	3.164	5.332
Shank	1.368	2.113	2.482	3.696	5.238
Belly	1.595	2.111	2.542	3.624	5.470
Neck	1.482	2.260	2.467	3.467	5.351

sides comprised the experimental lots and were lime-split to a thickness of 2.0 mm. In the first experiment both the control and experimental lots were processed together in the same drum. In the second experiment also the control and experimental lots were processed together but the extent of deliming in both lots was maintained at the same level. In the third experiment the control and experimental lots were processed in separate drums from the deliming stage to tanning. Lime split sides were delimed with less amount of deliming agent for a shorter time (with 0.25% ammonium chloride for 15 mt. only), pickled with less amount of sulphuric acid (1% on pelt weight) and tanned with slightly less amount of chrome extract p wder. After tanning the other operations were carried out in the same drum.

The qualities of the leathers obtained from sides split after tanning and after liming were examined visually and the observations are recorded in Table XVII.

Certain physical and chemical properties of the leathers produced in the thrid experiment were determined. Samples were taken from different areas of the hide in three pieces of leathers in each of the control and lime split lots in a direction parallel to backbone. Average values of the physical properties and chemical composition of the leathers are presented in Tables XVIII and XIX.

3.2. Discussion.

The change in Ts provides a good indication of the physico-chemical changes occuring in the hide during different tanning operations. It is apparent from Table XV that Ts in different areas of a wet salted or a soaked hide does not practically differ but during liming the decrease in Ts is much less in the butt area than in other areas. After 42 hr. of liming the decrease in Ts in shank, belly and neck areas is the same but comparatively high Ts is noted in butt area. This is expected as due to the compactness of the structure and thicknessof the area, penetration of lime is rather slow and also the extent of swelling is restricted resulting in a less extensive breakdown of the bonds

Table XVII

Leather quality of the sides split after liming and tanning

Experiment	Splitting after liming	Splitting after tanning
Experiment 1.	The quality of the leather was inferior to that of the control lot. The leathers were less full and of loose grain had raggy flanks	Leathers were of standard quality
Experiment 2.	The quality of the leathers was found improved when compared to that of leathers from the previous experiment. The leathers were good but found to be inferior to the control leathers. Variation in respect of different areas was still much more apparent than for control leathers	-do-
Experiment 3.	The leather quality was much better than that for experiment 2 and an overall assessment showed that the leathers were equally good or even better than the control lot. The variation in respect of positions was comparatively less.	-do

Table XVIII

Physical properties of experimental and 'control' leathers

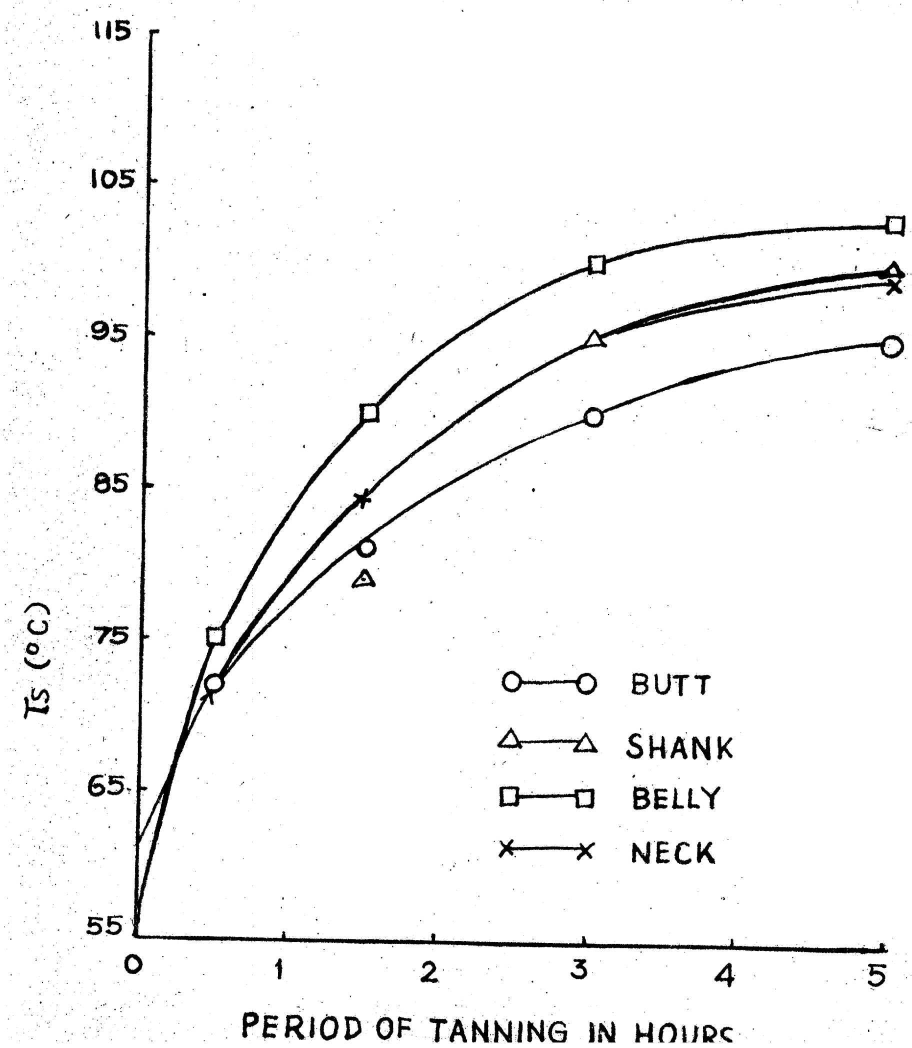
Physical properties (average of 3 sides)	Split after liming				Split after tanning			
	Butt	Shank	Belly	Neck	Butt	Shank	Belly	Neck
Tensile strength as lb./sq"	3252	6774	6766	8355	3578	6730	7440	8865
Tongue tear as lb./inch	291	308	200	242	293	321	200	246
Stitch tear as lb./inch	1272	1129	696	1093	1132	1221	807	892

TABLE XIX

Chemical properties of experimental and 'control' leathers

Chemical properties	Split after liming				Split after tanning			
	Butt	Shank	Belly	Neck	Butt	Shank	Belly	Neck
Moisture	16.60	16.80	17.80	15.50	17.20	18.10	18.20	17.90
Fat	2.64	3.05	2.88	2.75	2.40	3.15	2.72	2.32
Cr_2O_3	4.12	4.56	4.58	4.16	4.18	4.23	4.42	4.20
Hide substance	69.46	63.78	66.42	67.88	70.22	64.44	65.32	66.08

FIG: 7



115
105
95
85
75
65
55
Ts (°C)
0
1
2
3
4
5
PERIOD OF TANNING IN HOURS
BUTT
SHANK
BELLY
NECK

responsible for affecting Ts. After deliming, again the Ts becomes the same in all the areas. The extent of deliming is more in thinner and looser areas, the swelling is suppressed and the Ts increases to a considerable extent. But in the butt area the deliming is not complete, the swelling is repressed only partially and so the increase in Ts is somewhat less.

The increase in Ts during tanning has been presented in Fig. 6. It is apparent that during tanning for 3 hr. with 33% basic liquor the increase in Ts is comparatively higher in butt area than in other areas. Now, during early tanning the Ts of chrome tanned leather increases with increased chrome content[76]. As the increase in Ts is thus associated with higher chrome fixation the data tend to indicate that the rate of tanning is comparatively higher in butt area. But Fig. 7 representing the data of Table XVII, does not support this fact. On the contrary, it is found that increase in Ts during tanning is comparatively less in butt area than other thinner areas. The fixation of chrome by the butt area is thus expected to be minimum. Data presented in Table XVII confirm such a lower rate of chrome fixation in butt area. It is thus apparent that the rate of tanning is rather slow in butt area. The higher Ts in the butt area during tanning in the previous experiment may be attributed to the fact that pH of tanning in different hide areas were not identical or in other words, the pH of tanning was higher in the middle layer of butt area. As a result the basicity will increase and due to more chrome fixation the Ts will be increased[80]. This difference in the pH of tanning has resulted from the thickness and structural variation in different locations of the hide.

While considering the effect of lime splitting on the quality of finished leathers it may be seen that (Table XVIII) under normal processing the leathers produced from lime split hides are definitely inferior but when the process is carefully controlled or modified comparable or even better leathers can be produced from lime split hides. The leathers produced from lime-split sides after adjustment of the process are of tighter grain and have fuller flanks as compared to the control leathers. Rieger[46] expressed the view that during lime splitting the flanks and belly sections will be cut down further and when subjected to the bating enzymes they will be affected more than compact areas. This may, however, be possible while splitting heavier hides to the required minimum thickness. But in this experiment the hides used are not thick enough in the shank and belly areas to be cut down. So lime splitting to a thickness of approximately 2 mm will leave the shank and belly areas unaffected. Moreover, bating is not done in processing the sides into full chrome shoe upper leathers and so the lime-split sides are not expected to be affected by enzyme action.

Data presented in Table XIX indicate that there is no significant difference in the physical properties of the leathers produced from lime-split and control blue-split sides. Similar observations were also reported by Stainer et al[81]. These results may also be utilised in making a comparison between different locations in the leather in respect to physical strength. The results may be summarised as follows:

(i) The tensile strength appears to be the least in butt area and maximum in the neck area.
(ii) Belly region seems to possess the minimum tongue tear strength and the shank area appear to have maximum tongue tear strength. Tongue tear strength in butt area is very close to that of shank area.
(iii) Stitch tear strength is the least in belly area. Butt and shank areas possess roughly the same stitch tear strength.
(iv) Physical properties of the leathers are independent of variation in thickness.

The tensile strength of leather was found to vary greatly over the entire area of the leather[51] [82]. The low tensile strength in butt area is not unexpected and may be due to more compact structure in the butt area which prevents the fibres to slip as in the case of looser areas. Secondly splitting of the hide either in the lime or in the blue stage is also responsible for such effect as it was shown that[83] [84] the strength of leather decreases greatly depending on the extent of splitting. As the thicker areas are split to a greater depth the strength of these areas is also affected appreciably.

The chemical properties of the leathers (Table XX) are also unaffected by splitting variation. However, the chemical composition of the leather may differ in different locations to some extent. Wilson[53] reported that certain chemical properties of chrome tanned calf skin may vary in the butt and belly areas due to the influence of structural variation in these areas. The slightly higher values for moisture, fat and Cr_2O_3 in the shank and belly areas are probably due to the influence of both thickness and structural variation in those areas.

4. Effect of delay in cure of buffalo hide on the rate of vegetable tanning and on the properties of sole leather.

4.1. Experimental procedure and results.

A freshly slaughtered buffalo hide was taken from slaughter house, washed, green fleshed and then cut into experimental samples as shown in Fig. 8. Hide samples (taken in pile flesh side up) were keptinside a moist chamber at room temperature (29°C ± 1°C) for staling. Samples were taken out after 24, 48 and 64 hours' staling, sprayed with an antiseptic solution (Topane WS, I.C.I.) and then salted with common salt. Salted hides were stored for a period of 7 weeks and then taken for quality assessment and tanning. Samples I, II, III and IV staled for different periods, were taken for the quantitative determination of hide quality. Data on hide quality are given in Table XX.

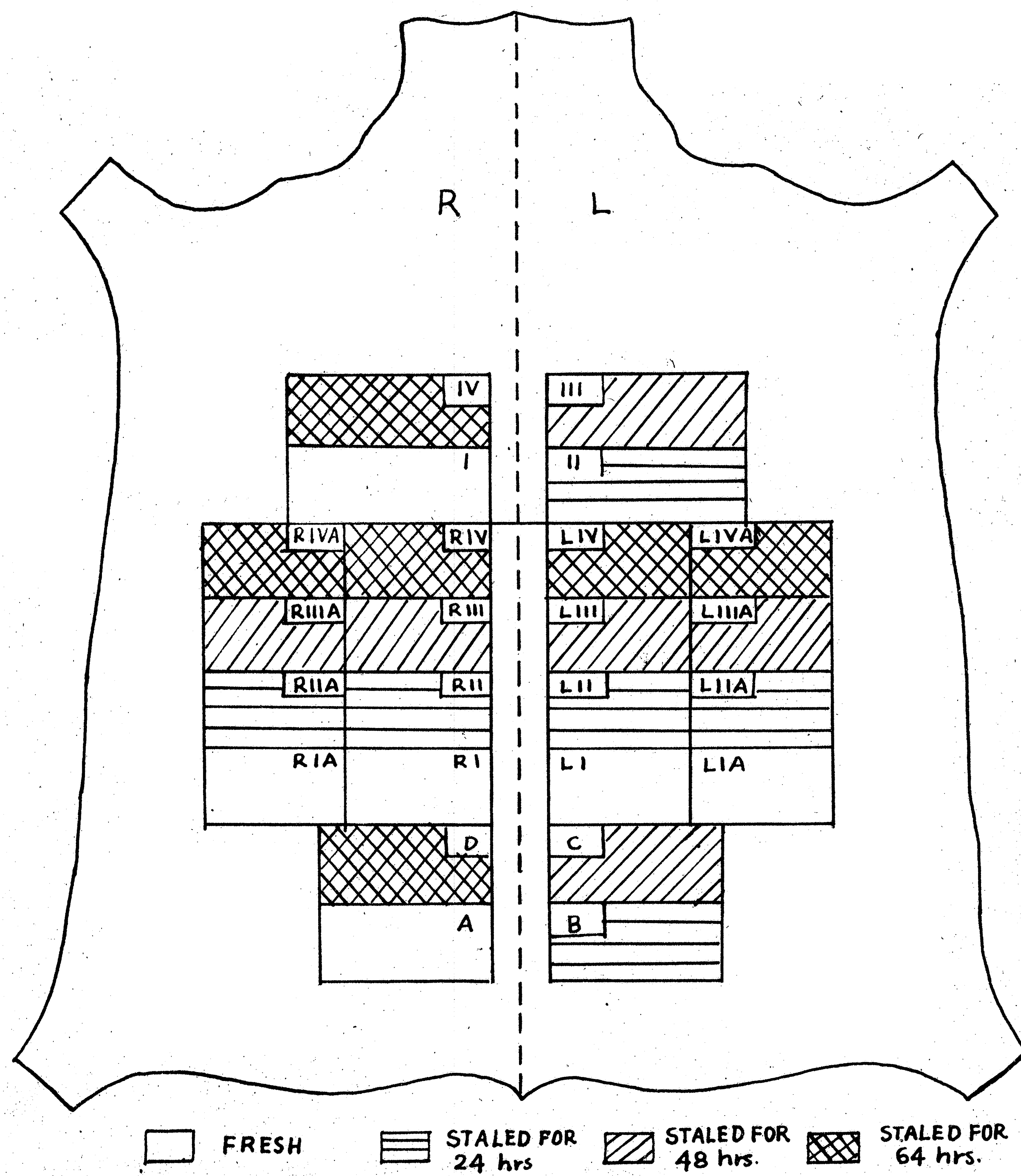
Samples A, B, C and D were taken to study the effect of staling on the rate of tanning. Samples RI, RIA; RII, RIIA; RIII, RIIIA; RIV, RIVA, staled

TABLE XX

Quantitative assessment of hide quality as affected by delay in cure

Period of staling (hr.)	Hair-slip	Extractable hydroxy-proline (% of total N)
Fresh	No	0.002
24	No	0.002
48	Yes	0.021
64	Yes	0.038

FIG_8


R
L
IV
I
III
II
RIVA
RIV
LIV
LIVA
RIIIA
RIII
LIII
LIIIA
RIIA
RII
LII
LIIA
RIA
RI
LI
LIA
D
A
C
B
FRESH
STALED FOR 24 hrs
STALED FOR 48 hrs.
STALED FOR 64 hrs.

for varying periods were considered as experimental samples and the corresponding fresh samples from the left side were taken as control ones. These samples were used to study the weight yield and certain physical and chemical properties of the leathers.

Hide samples were soaked, limed for 7 days, delimed completely and then tanned according to the procedure mentioned earlier. The pelt tan liquor ratio used was 1:10. Extent of tannage was measured from Ts and fixed tan determination at regular intervals and the data obtained are given in Tables XXI and XXII.

The weight yield of leather calculated as percent on green, staled and pelt weight are presented in Table XXIII. Data given in the table are the average values obtained from two samples in each case.

Certain physical and chemical properties of the leathers obtained from staled and control fresh samples are tabulated in Tables XXIV and XXV.

4.2 <u>Discussion</u>

Extractable hydroxyproline nitrogen present in hide samples (Table XXI) show that fresh and 24 hr. staled hides, stored for a period of 7 wk. after salting, are capable of producing good leathers but the hide samples staled for 48 and 64 hr. are deteriorated in quality to a considerable extent and only poor quality leathers can be produced out of such staled hides.

It is apparent from Table XXII that the rate of tanning is comparatively slow in case of fresh hide where the maximum Ts has attained after 8 days' tannage. In case of the staled hide samples maximum Ts has reached after 6 days although plotting of the data may show that the rate of tanning slightly increases with the increase in staling period.

Data on tannin fixation reveal that the rate of tanning, independent of staling period, is quite rapid during the early stages of tanning (upto 6 days) after which the rate of tannin fixation is rather slow. This is due to the combination of a part of diffusible tannin

TABLE XXI

Effect of staling of buffalo hide on the rate of vegetable tanning as determined by Ts°C.

Strength of tan liquor (°Bk)	Fresh	Period of staling 24 hrs.	48 hrs.	64 hrs.
Delimed	0	0	0	0
10 (2d)	6.0	7.0	6.5	6.0
20 (4d)	15.0	18.5	21.5	23.5
30 (6d)	22.0	24.0	24.5	24.5
40 (8d)	23.5	23.0	23.5	24.0
60 (10d)	21.0	21.0	21.0	22.5
80 (12d)	19.5	20.0	19.5	20.0
100 (14d)	18.0	18.0	18.5	19.0

TABLE XXII

Effect of staling of buffalo hide on the rate of vegetable tanning as determined from tannin fixation.

(% fixed tan on dry weight)

Strength of tan liquor (°Bk)	Fresh	Period of staling		
		24 hrs.	48 hrs.	64 hrs.
Delimed	0	0	0	0
10	30.03	33.76	35.62	37.15
20	40.41	41.89	43.41	43.43
30	47.39	48.52	49.29	48.62
40	48.44	50.18	48.48	48.10
60	48.15	48.45	48.80	48.50
80	48.72	49.89	49.02	49.07
100	49.68	50.53	51.72	52.62

TABLE XXIII

Effect of staling of buffalo hide on the weight yield of vegetable tanned leather*

Period of staling (hr.)		Weight yield of leather (%) Calculated on green wt.	Calculated on staled wt.	Calculated on pelt wt.
Fresh	Experiment	79.68	79.68	66.90
	Control	80.07	80.07	66.37
	Variation	0.39	-0.39	+ 0.53
24	Experimental	78.32	79.29	66.56
	Control	78.04	78.04	66.22
	Variation	+0.28	+ 1.15	+ 0.34
48	Experimental	68.67	72.16	62.87
	Control	76.25	76.25	65.04
	Variation	7.58	- 4.09	- 2.17
64	Experimental	65.63	69.19	81.42
	Control	76.59	76.59	66.36
	Variation	10.96	- 7.40	-4.94

*Average yield of two samples are presented in each case.

+ = More than control; - = Less than control

Table XXIV

Effect of staling of buffalo hide on some physical properties of finished sole leather

Physical properties (Average of two samples)		Fresh	Period of staling (hr.) 24	48	64
Abrasion (inch/ 400R)	Control	0.093	0.102	0.102	0.095
	Experimental	0.084	0.093	0.092	0.062
	Difference	- 0.009	- 0.009	-0.010	- 0.033
Water absorption (%)	Control ½ hr.	31.4	30.2	32.9	32.8
	24 hr.	45.8	46.1	45.1	46.1
	Experimental ½ hr.	31.2	29.7	38.4	42.9
	24 hr.	46.2	45.9	50.2	52.6
	Difference ½ hr.	-0.2	-0.3	+5.5	+10.1
	24 hr.	+0.4	-0.2	+5.1	+6.5
Apparent density	Control	0.987	0.987	0.990	0.998
	Experimental	1.018	1.000	0.977	0.975
	Difference	+0.031	+0.013	-0.013	-0.023
Apparent density x Hide substance	Control	40.27	40.17	39.60	40.12
	Experimental	41.23	40.10	38.10	37.54
	Difference	+0.96	-0.07	-1.50	-2.58

\+ More than control

\- Less than control

TABLE XXV

Effect of staling of buffalo hide on the chemical composition of sole leather

Chemical analysis		Fresh	Period of staling		
			24 hrs.	48 hrs.	64 hrs.
Moisture	Control	12.9	12.7	12.7	13.2
	Experimental	12.3	12.7	12.5	12.6
Oils and fats	Control	2.2	2.1	2.2	2.6
	Experimental	2.2	2.2	3.4	2.2
Water solubles	Control	17.8	17.8	17.4	17.0
	Experimental	18.0	17.7	18.0	18.4
Hide substance	Control	40.8	40.7	40.0	40.2
	Experimental	40.5	40.1	39.0	38.5
Degree of tannage	Control	64.5	65.6	69.3	67.1
	Experimental	66.7	67.6	72.1	73.5

As regards apparent density, no significant difference can be noted between the experimental and control leathers. It is expected that an empty fibre structure will show less apparent density but during vegetable tanning a pelt with loose fibre structure will absorb more water solubles. The density of the water solubles being roughly the same as that of fibres, the possible decrease in apparent density in leathers from highly staled hides seems to be mostly compensated. Bradly[87] pointed out that the assessment of structure may better be based upon the product of percentage hide substance and apparent density. A comparison of such values (products of hide substance and apparent density) between the control and experimental leathers shows that hide structure is affected by considerable delay in cure.

It is striking to note that abrasion of the leathers is not influenced upto 48 hr. staling but seems to be less in leathers from 64 hr. staled hides. While comparing the properties of sole leathers made from staled and fresh hide Robertson[48] observed that bend samples from most of the staled side possessed surprisingly good resistance to abrasion. Staled belly samples, however, showed lower abrasion resistance. This high abrasion resistance was explained by her due to bacterial degradation during staling which resulted in glueing together of the corium fibres during manufacturing process.

While comparing the chemical composition of the control and experimental leathers (Table XXVI) it may be noted that water solubles slightly increase and hide substance slightly decreases with the increase in staling period. Degree of tannage appears to be slightly higher in case of highly staled hide.

General appearance and assessment of the leathers are found to be normal upto 24 hr. staling but are affected due to considerable grain damage and may be graded only as rejections when staled for 48 hr. or more. Flexibility is also found to be influenced by staling; leathers from 48 and 64 hr. staled hides appear to be somewhat soft.

It is thus apparent from the present investigation that sole leather making potentiality of buffalo hide remains unaffected upto 24 hr. staling and then deteriorates progressively with the increase in staling period.

5. Effect of area-wise variation in buffalo hide on the rate of tanning and on the properties of sole leather

5.1 Experimental procedure and results

A freshly slaughtered buffalo hide was washed, green fleshed and then cured by wet salting. After piling for one week the hide was soaked, limed, delimed completely as before and then cut into two sides. Samples were then cut from the right hand side according to Fig.9. The side was cut into three segments A,B & C in lines, parallel to backbone. Segment A was then cut into 10 pieces, segment B was cut into 8 pieces and segment C into 7 pieces. The entire side was thus divided into 25 pieces each measuring roughly 28 cm x 18 cm. These samples were utilised to study th variation in rate of tannage in different locations. Both Ts and fixed tan were determined at regular intervals during tannage as in the previous occasion. The results obtained are presented in Figs.9 and 10 and in Table XXVI.

It is apparent from Fig.9 that the tanning time required to get maximum Ts gradually decreases in each of the segments from the tail end of the hide to the neck and except in position 10A, i.e. in area just near the head. The extent of variation throughout the side is quite appreciable and ranges from 6 days to 12 days. The rate of tanning from chemical crosslinking point of view, appears to be most rapid in sampling positions C6 and C7 and most slow in positions B1, B2, B3 and B4.

According to fixed tan data presented in Table XXVI the rate of tanning appears to be comparatively rapid in samples A6 to A9 in segment A, in samples B6 to B8 in segment B and in samples C5 to C7 in segment C during early stages of tanning i.e. upto about 8-10 days tanning. The rate of tannin fixation is most rapid in samples C6 and C7 and comparatively slow in samples B1 to B5.

FIG_9

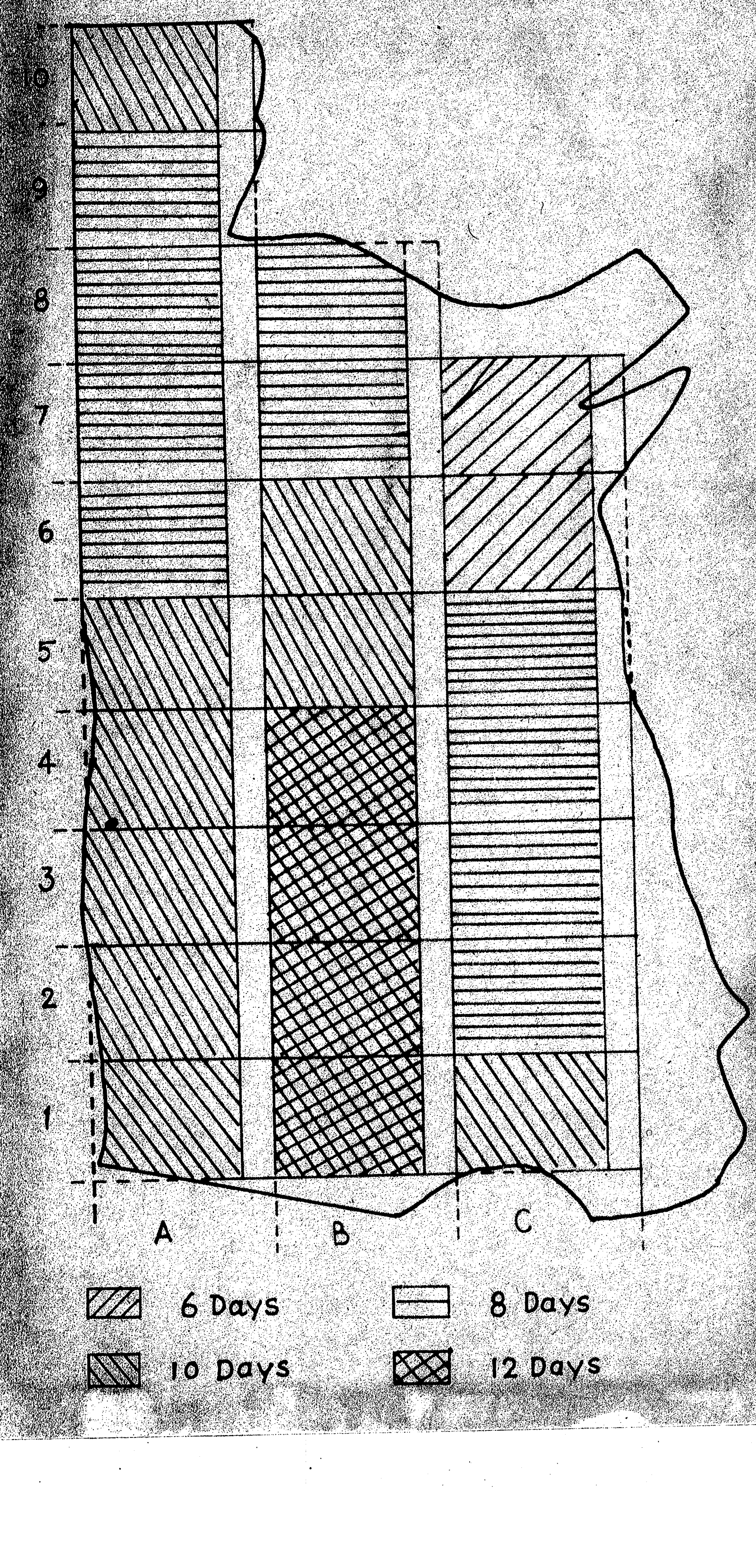
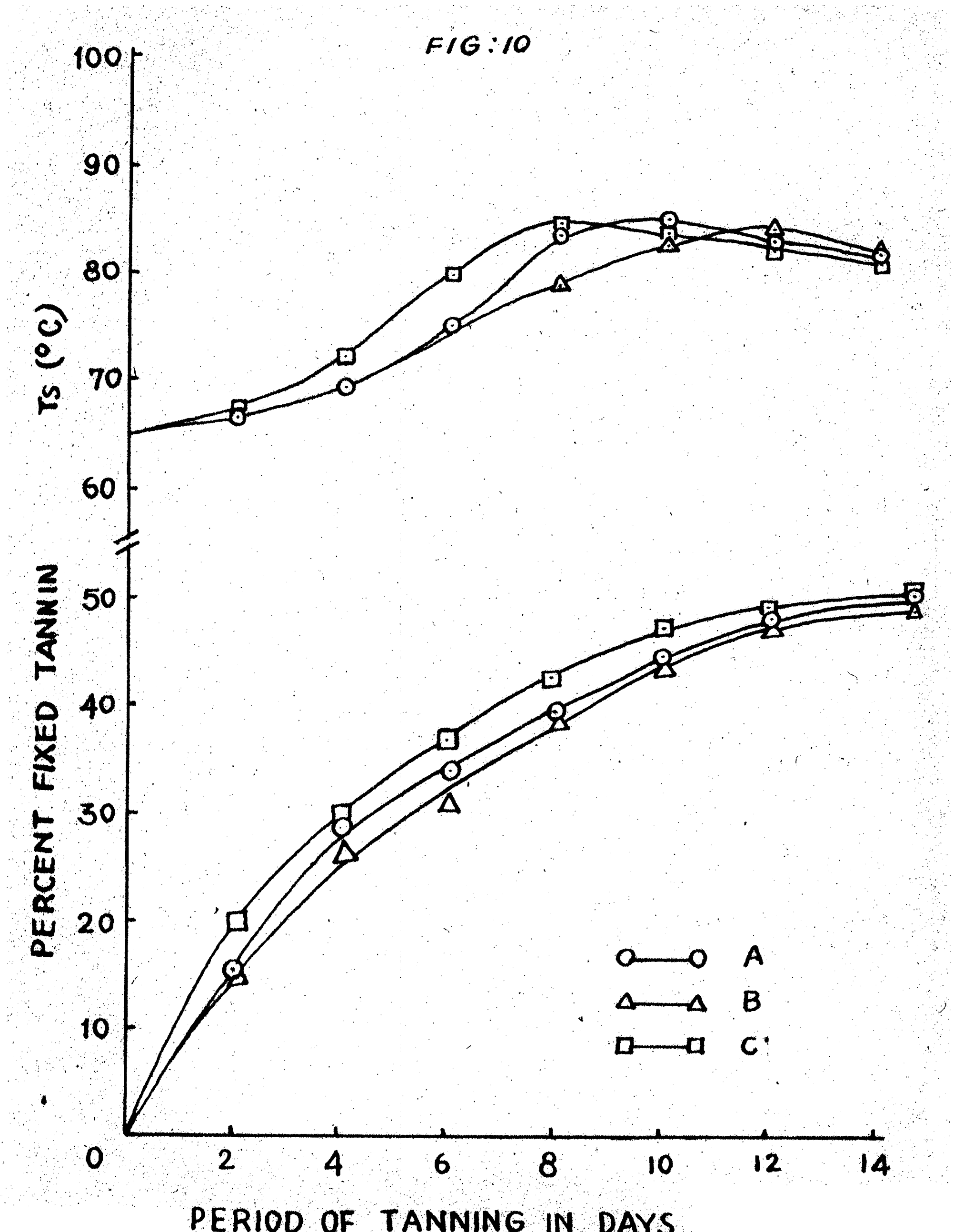


FIG : 10



100
90
80
70
60
50
40
30
20
10
0
Ts (°C)
PERCENT FIXED TANNIN
2
4
6
8
10
12
14
PERIOD OF TANNING IN DAYS
A
B
C

Table XXVI

Effect of areawise variation in buffalo hide on the rate of vegetable tanning as determined by fixation of tannin (% fixed tan on dry weight)

Location in hide	Strength of tan liquor						
	2 days 10°Bk	4 days 20°Bk	6 days 30°Bk	8 days 40°Bk	10 days 60°Bk	12 days 80°Bk	14 days 100°Bk
A1	13.5	26.1	29.6	34.9	43.9	47.1	48.2
A2	14.2	30.5	35.6	38.4	44.3	46.4	51.0
A3	14.0	26.0	30.4	36.0	45.1	46.1	50.7
A4	11.0	24.0	32.8	39.1	44.2	47.2	50.0
A5	11.3	27.9	36.6	39.8	43.2	48.2	51.0
A6	16.2	30.5	37.9	41.7	44.9	47.5	49.8
A7	18.6	31.4	38.1	41.8	44.8	48.9	49.1
A8	19.6	28.7	34.8	39.6	45.0	49.0	51.3
A9	18.5	31.6	34.9	40.7	43.3	49.4	50.9
A10	17.7	28.0	30.1	38.6	43.5	48.9	49.5
B1	14.6	23.2	25.9	37.2	43.7	46.7	48.5
B2	15.8	21.8	24.7	38.4	43.2	47.3	47.5
B3	14.6	26.8	29.3	38.4	43.3	46.0	47.3
B4	14.1	24.0	27.9	38.1	40.5	46.1	48.0
B5	11.0	22.8	29.9	36.8	43.4	46.7	50.0
B6	16.4	26.2	34.5	38.4	46.0	48.9	50.2
B7	17.6	30.7	37.7	40.7	45.3	47.1	49.4
B8	16.7	31.8	37.8	39.9	45.3	49.1	49.7
C1	16.6	25.2	34.9	36.9	46.1	48.3	50.2
C2	20.7	28.8	34.8	40.9	47.6	47.7	49.9
C3	19.0	23.1	32.8	42.9	45.9	47.7	50.5
C4	16.0	25.4	36.0	41.9	46.4	50.2	52.5
C5	22.7	25.1	38.1	42.2	46.7	48.7	50.7
C6	20.4	33.6	39.9	43.3	47.5	49.9	51.1
C7	24.7	34.7	41.2	46.5	48.6	49.7	51.0

Whether the thickness or structural variation influences more on the rate of tanning was examined in a separate experiment. Three samples were taken from a limed buffalo hide from positions identical with B5, B6 and C6. Samples B6 and C6 were splitted to the same thickness (5 mm.). Sample B5 was not splitted (6.2 mm). The samples were then delimed and tanned as usual and the rate of tanning was determined from Ts determination. Data obtained are presented in Table XXVII.

It may be noted from Table XXVII that the rate of tanning does not differ significantly between two positions (B6 and C6) having the same thickness but structural variation. On the other hand, the rate of tanning is found to be affected when the thickness varies considerably having roughly the same structure (B5 and B6).

A small strip of hide was cut from each of the samples (white portions in Fig.9) and were dehydrated by treating with increasing concentrations of acetone. The apparent density of these dried pelts were determined and reported in Table XXVIII.

Apparent density of the acetone dried delimed pelts seems to increase slightly from the tail end in segment A but in segments B and C the extent of variation is not very significant.

The left hand side of the hide was cut into identical 25 samples as in right side and the samples were used for measuring thickness variation throughout the side, weight and area yield of leather and for the determination of certain physical properties of leather. Thickness was measured in 12 positions along the breadth of the side and in 20 - 14 positions throughout the length. The variation in thickness of delimed pelt is shown in Fig.11.

An analysis of the average values for thickness in each sample shows that thickness of the pelt gradually decreases from the tail end towards the neck in segments B and C. But in segment A, there is not much variation in thickness in samples A1 to A6, then the thickness decreases in samples A7 and A8 and then again increases in samples A9 and A10.

TABLE XXVII

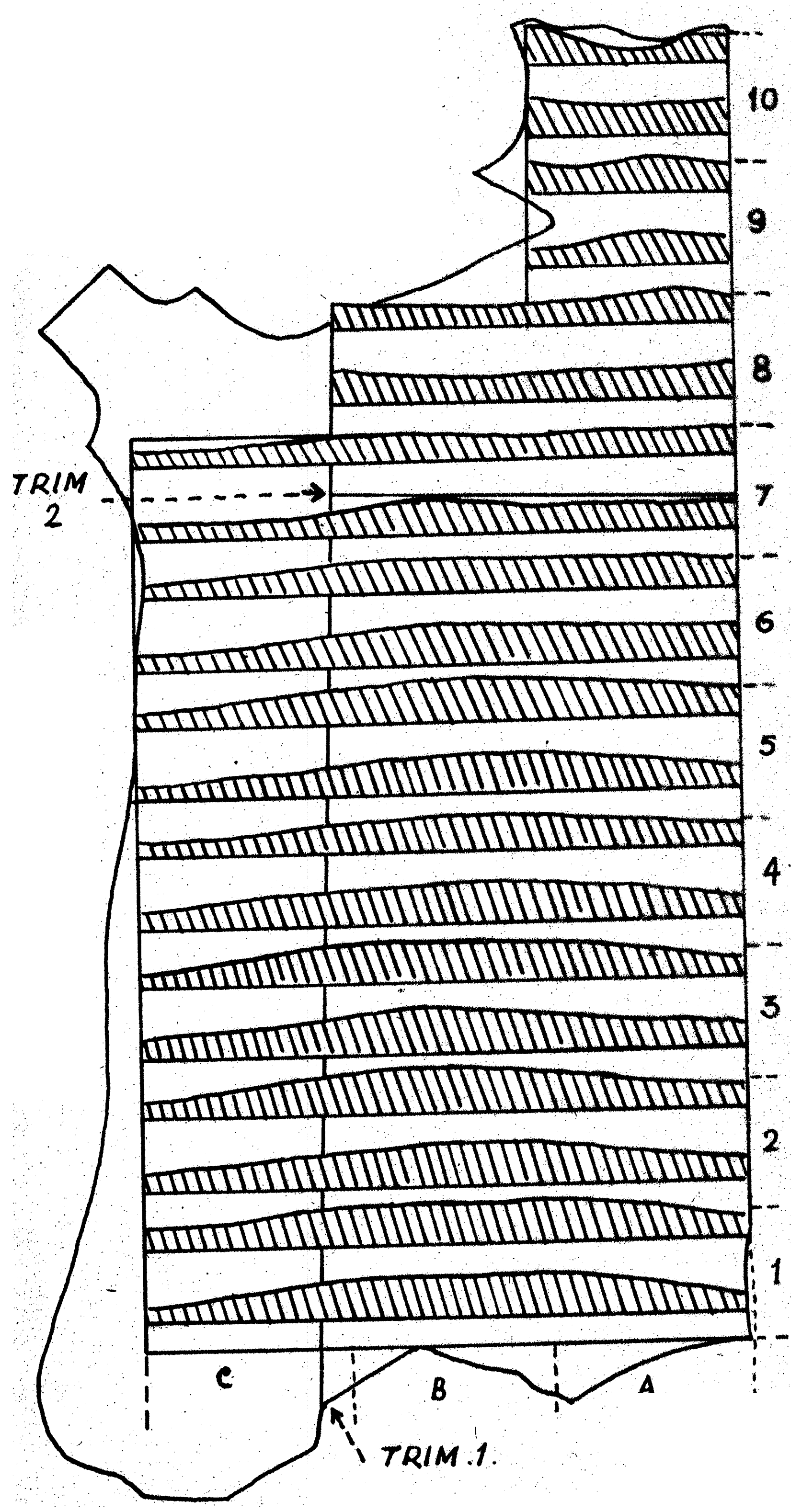
Effect of thickness and structural variation in buffalo hide on the rate of tanning as determined by Ts.

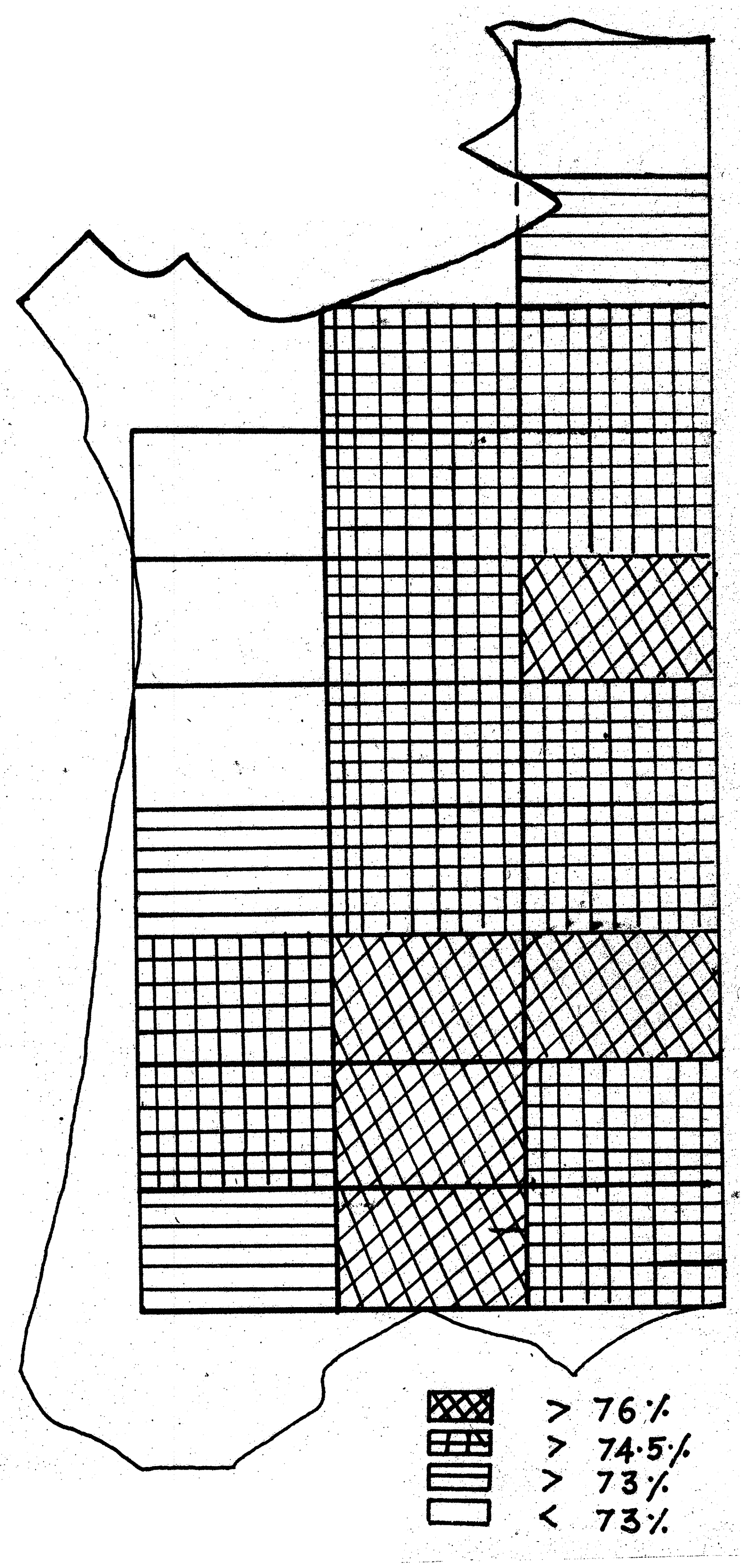
Location in hide	Delimed pelt	Increase in Ts (°C)						
		10 2 Days	20 4 Days	30 6 Days	40 8 Days	60 10 Days	80 12 Days	100 14 Days
B 5 (Not splitted)	0	1.5	6.5	15.5	23.5	22.5	20.0	18.0
B 6 (splitted)	0	5.5	14.5	25.0	23.0	21.5	19.5	18.5
C 6	0	5.5	15.5	24.0	22.5	21.0	18.5	17.5

Table XXVIII

Variation in area yield (% on delimed area) of leather in different locations of the buffalo hide

Location in hide	Area yield of leather before rolling and finishing	Area yield of finished leather
A1	2.06	3.61
A2	1.56	3.05
A3	1.98	3.98
A4	2.26	4.68
A5	2.96	4.83
A6	2.03	4.37
A7	2.97	4.81
A8	3.00	4.84
A9	3.26	5.09
A10	0.96	2.00
Average	2.30	4.13
B1	3.54	7.08
B2	2.69	6.83
B3	2.92	6.53
B4	3.20	5.32
B5	3.14	4.79
B6	2.01	4.61
B7	1.65	3.61
B8	2.29	3.36
Average	2.68	5.27
C1	2.71	4.04
C2	1.18	2.71
C3	2.77	4.27
C4	0.81	2.49
C5	2.28	3.33
C6	0.89	2.14
C7	1.51	2.45
Average	1.74	3.06


10
9
8
7
6
5
4
3
2
1
TRIM 2
C
B
A
TRIM 1.


> 76%
> 74.5%
> 73%
< 73%

The variation in weight yield of finished leather samples in different locations of the side is presented in Fig.12.

It is apparent from Fig.12 that leather yield (weight) varies to some extent depending on the area of the hide. The extent of variation in weight yield ranges from 71.6 - 77.4 percent on delimed pelt weight. To have a better understanding the entire range of variation has been divided into 4 groups. The trend of variation between the samples of each segment does not appear to be quite regular as in case of rate of tanning. But it is quite apparent that thinner samples e.g. C7, C6 and C5 have given lesser yield and the thicker positions B1, B2 and B3 have produced higher weight yield of leather. Sample 10A seems to be an exception.

Area yield of leather (calculated on delimed pelt area) after tanning and after rolling and finishing were determined in different sampling positions and the data obtained are presented in Table XXIX.

Like that of weight yield, area yield of finished leather samples (on delimed area) appears to vary in different locations the range of variation being about 102 - 107%. In segment A, area yield is slightly less in samples A1, A2 and A3 than the other samples where there is not much variation between them. Here again sample A10 is an exception. In samples of segment B, area yield decreases as the samples approach the neck region. The variation in area yield in samples of segment C is somewhat irregular but appears to be slightly decreasing from the hind to the fore leg. Samples B1, B2 and B3 are found to give significantly higher area yield in the entire side.

Before rolling and finishing, however, the extent of variation in area yield throughout the side is not very significant (i.e. 101 - 103% roughly). This shows that rolling of leather may considerably influence the area yield of leather. Probably thickness variation has got more bearing on increase in area yield during rolling and so the area increases after rolling by about 100% in thicker samples like B1, B2 and B3.

Table XXIX

Apparent density of acetone dehydrated delimed pelt

Sample No.	Location A	B	C
1	0.63	0.72	0.85
2	0.63	0.68	0.83
3	0.66	0.70	0.87
4	0.66	0.66	0.78
5	0.67	0.69	0.79
6	0.65	0.66	0.91
7	0.71	0.72	0.89
8	0.79	0.76	
9	0.78		
10	0.72		
Average	0.69	0.70	0.85

Water absorption, apparent density, abrasion and tensile strength of the leather samples from different locations are given in Table XXX.

Data presented in Table XXX indicates the trend and extent of variation of physical properties in different sampling positions. In samples of segment A, water absorption does not differ much in samples A1 to A6 but appears to be more in samples A7 - A10. In samples of segment B water absorption gradually increases from B1 to B8 in three stages and in samples of segment C water absorption varies slightly in samples C1 to C5 but increases considerably in C6 and C7.

Apparent density of the samples of A segment varies slightly with a tendency to diminish in value from the tail to the neck end. Samples in segment B have roughly the same apparent density and in segment C it may vary to small extent.

Abrasion in samples of all the segments varies to certain extent but no trend of variation can be noted in between the samples.

Areawise variation in hide also influences the tensile strength of sole leather although there exists no correlation between tensile strength and thickness or structural compactness.

5.2 Discussion

The extent of variation in rate of tanning and in other properties of sole leather between the samples of each of the segments A, B and C has already been dealt with. The difference between the average values of the samples in the three segments may provide with more comprehensive views about the influence of locational variation. Fig.9 gives a topographical picture of the variation in tanning time that is required for the completion of tannin penetration and of crosslinking formation in different areas of the hide during tanning. It is, however, difficult to compare the data on tannin fixation (Table XIII) in between the samples of each segments but an analysis of the data broadly shows certain variations in tannin fixation and the trend of variation in tannin fixation corroborates with the trend as indicated by Ts data. The average values

Table XXX

Effect of areawise variation in buffalo hide on certain physical properties of sole leather

Location in hide	Water absorption(%) ½ hr	24 hrs.	Apparent density	abrasion (in./400 R)	Tensile strength (lb./sq.inch)
A1	33.6	42.2	0.92	0.064	4889
A2	34.7	44.5	0.91	0.063	7008
A3	35.6	41.4	0.88	0.079	5786
A4	42.4	48.6	0.90	0.071	5594
A5	38.2	43.4	0.89	0.074	5375
A6	43.1	48.7	0.87	0.069	5341
A7	44.2	53.2	0.85	0.075	5880
A8	40.1	52.2	0.87	0.079	4049
A9	38.9	54.5	0.88	0.086	4360
A10	39.9	56.8	0.81	0.085	3957
Average	39.1	48.6	0.88	0.075	5224
B1	34.1	42.4	0.92	0.071	5780
B2	35.5	42.1	0.89	0.075	5382
B3	34.0	43.4	0.91	0.082	5927
B4	37.8	47.2	0.91	0.067	5043
B5	41.0	47.4	0.91	0.082	5039
B6	35.5	47.0	0.90	0.072	6064
B7	39.3	48.0	0.90	0.070	5672
B8	38.3	49.5	0.91	0.078	5079
Average	36.9	45.9	0.91	0.075	5498
C1	39.7	57.8	0.87	0.074	5471
C2	36.8	56.8	0.88	0.075	4248
C3	41.9	53.7	0.83	0.090	4962
C4	50.2	61.0	0.87	0.082	4455
C5	44.0	56.2	0.83	0.073	5430
C6	52.7	64.6	0.84	0.073	5955
C7	53.6	65.6	0.85	0.63	5788
Average	45.6	58.7	0.85	0.078	5184

for Ts and fixed tan of the samples in segments A,B and C that are obtained in the course of tanning are presented graphically in Fig.10. The extent of variation in rate of tanning is quite apparent and are found to decrease in the following order C > A > B.

It may be noted that the trend of variation in rate of tanning or in tanning time in different areas of the hide bears a good correlation with thickness variation in the delimed pelt. This is further supported from the data in Table XXVIII. Although the rate of tanning is found to be affected more by thickness variation in influence of structural variation cannot be completely ignored.

The average leather yield (weight) of the samples in segments A, B and C decreases in the following order B(76.14%) > A(75.08%) > C(73.5%). This trend of variation may, however, be compared well with the variation in average thickness of the samples in the segments e.g. B(4.89 mm) > A(4.24) > C(3.34).

The average area yield of the leathers in the three segments also varies in the same decreasing order as in weight yield. It has already been mentioned that increase in area yield (on delimed area) is only little before rolling and finishing but after rolling area yield increases further and the difference in area yield is also more prominent. On an average, the area increase of leather by rolling is more in segment B and less in segment C.

While comparing the average physical properties of the leather samples in the three segments it may be noted that water absorption is the lowest in segment B, in segment A, it slightly increases but in segment C it increases to a greater extent. Mitton[88] pointed out that water absorption varied in different locations of the leather and a higher water absorption of leather is indicative of its loose and open structure. The present water absorption data are therefore likely to give an indication about the structural variation in hide and leather.

Average values for apparent density do not differ much between the segments although the trend of variation is in the following direction B > A > C. According to Mitton the extent of variation in apparent density throughout the leather was less marked than it is expected to be. This is because looser areas of the hide absorb more water soluble materials having roughly the same density.

The trend of variation in apparent density of acetone dehydrated delimed pelt is somewhat striking. Average apparent density values of samples in segment C appears to be significantly higher than that of segments A and B. It may be noted that there exists no direct correlation between the apparent densities of acetone dehydrated pelts and finished sole leathers. It may be possible that by acetone dehydration the volumes of the loose textured samples in segment C are reduced more thus leading to an increase in apparent density. On the other hand, the apparent density of finished leather depends on both the densities of fibre and tannin materials including water solubles.

Average abrasion values appear to be slightly more in segment C whereas in segments A and B these values are roughly the same.

Average values for tensile strengths are roughly the same in all the segments.

The present investigation therefore reveals that the leather making potentiality of the samples of segment C are rather poor for vegetable tanned sole leather. They are thin, give less weight and area yield, absorb more water and have slightly less apparent density. To produce better and uniform sole leather it would therefore be better to trim out the hide as shown in Fig.11 (trim 1); sample A10 is also unsuitable for any good quality leather. More attention are to be paid to the locational variation in hide or leather when manufacture of industrial leather from buffalo hide is concerned. Samples A7, A8, A9 and B7 and B8 may not be quite suitable as they are comparatively thin, less compact in structure, have comparatively more water absorption and samples A8 and A9 have lower tensile strength. Buffalo hide may therefore be further trimmed (trim 2) as shown in Fig.11 to produce industrial leather of uniform quality.

6. Effect of precuring extraction of hide, type of cure and pretanning operations on the rate of tanning and on properties of sole leather.

6.1. Experimental procedure and results.

Freshly slaughtered buffalo hides (wt. range 45-50 lb.) were collected from slaughter house, washed to remove blood, dirt, etc., green fleshed and then cut into experimental pieces according to fig. 13.

6.1.1. Effect of precuring and pretanning extraction.

Hide pieces from left hand side of the hide were taken as experimental samples and from right hand side as control samples.

(i) Green hide samples LI and LIA were taken in polyethylene bags and kept in the deep freeze (-30°C) in green condition till they were processed. The samples were soaked in water to defreeze them, shaved on the grain surface with a safety razor and then taken directly for tanning. Thecorresponding control samples (RI and RIA) were green salted and piled for a period of 10 days. They were soaked well, limed for 7 days as mentioned earlier, delimed completely and then taken for tanning.

(ii) Extracted with sodium chloride solution:

Samples L2 and L2A and R2, R2A were extracted three times with 10% salt solution in a plastic drum running the drum for 1 hr. in each extraction. Hide and salt solution ratio used was 1:5. After extraction samples L2 and L2A were washed in water to remove salt and then stored in the deep freeeze. The samples were later soaked, unhaired with the help of a razor, the epidermal layer was then removed mechanically with a blunt knife. They were then washed again and taken for tanning. Control samples were green salted after extraction with salt and then kept in pile. They were processed as in RI and RIA.

(iii) Extraction with sodium chloride solution and then with half saturated calcium hydroxide solution:

Samples L3 and L3A and also R3 and R3A were first extracted with 10% salt solution as in (ii) and then extracted thrice with half saturated lime solution drumming them for 1 hr. in each occasion. Hide and half saturated lime liquor was taken in the ratio of 1:5. After extraction the experimental samples L3 and L3A were washed well with water, neutralised with ammonium sulphate and then kept in the deep freeze. During processing the samples were soaked in water, unhaired with a blunt knife, washed and then put to the tan liquor. The control samples were green salted and then kept in pile. They were processed as other control samples.

Tanning was done as before and the rate of tanning was determined from the rate of increase of Ts.* Data obtained are presented in Table XXXI.

As expected, the rate of tanning is appreciably delayed in fresh hide (no liming) and the penetration of tanning is found to be incomplete even after 14 days' tanning. Maximum Ts is attained after treating them for an additional 2 days at 100° Bk. liquor. The rate of tanning is quickened by salt extraction of the hide and the maximum Ts is reached after 12 days. After extraction of the hide with salt plus lime solution tanning rate may increase very slightly but 12 days' tanning is required for maximum Ts as in case of salt extracted samples.

In case of control samples (processed normally after extraction), the rate of tanning is found unaffected by salt or salt plus lime extraction and the maximum Ts is obtained after 10 days period.

The effect of precuring extraction of hide on leather yield may be noted from Table XXXII.

It appears that extraction of hide prior to tanning may improve on the leather yield to some extent. This trend of variation is also present in control samples which were extracted prior to curing, but the extent of variation is not significant. But it is striking to note that leather yields of the experimental samples are not affected at all in comparison to that of control samples although it was expected that liming of the hide will result in higher yield because of removal of the

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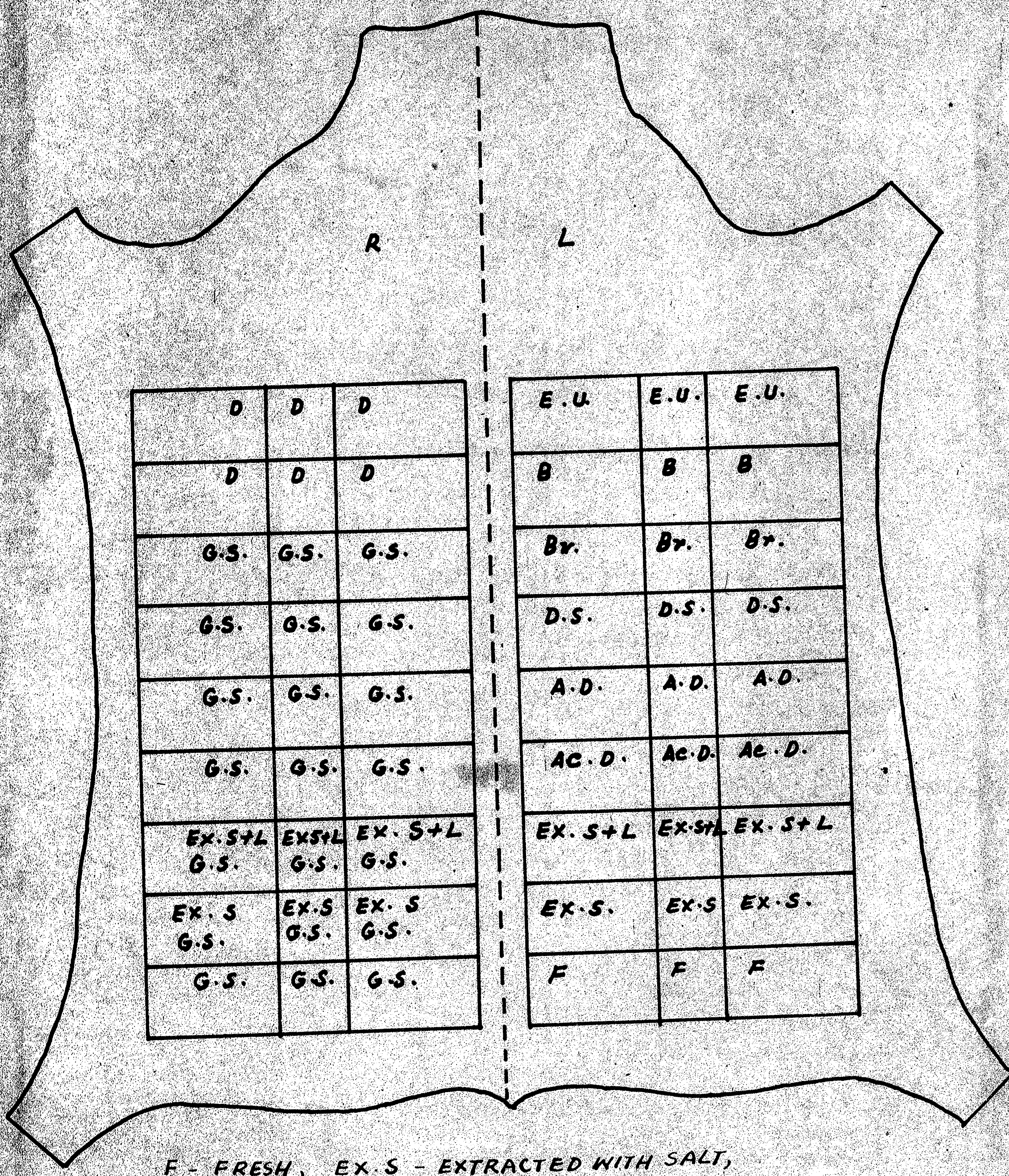
FIG: 13



F - FRESH, EX.S - EXTRACTED WITH SALT,
EX.S+L - EXTRACTED WITH SALT + LIME,
G.S - GREEN SALTED, AC.D - ACETONE DRIED,
A.D - AIR DRIED, D.S - DRY SALTED,
BR - BRINED, D - DELIMED, B - BATED
E.U - ENZYME UNHAIRED.

Table XXXI

Effect of extraction of hide prior to curing and tanning on the rate of vegetable tanning as determined by Ts.

Treatment of hide		Increase in Ts(°C)							
		Delimed Pelt	10°Bk 2 d.	20°Bk 4 d.	30°Bk 6 d.	40°Bk 8 d.	60°Bk 10 d.	80°Bk 12 d.	100°Bk 14 d.
Fresh hide	Control	0	3.5	5.5	11.0	19.5	22.0	21.5	19.5
	Experimental	0	0	0.5	2.0	2.5	6.0	15.0	16.0
Extracted with 10% NaCl solution	Control	0	3.0	4.5	10.5	19.5	22.5	22.0	20.0
	Experimental	0	1.0	2.0	3.0	4.5	15.0	18.5	17.0
Extracted with 10% NaCl solution + half saturated lime solution	Control	0	2.5	6.0	12.5	19.5	22.5	22.0	20.0
	Experimental	0	2.0	3.0	3.5	10.0	16.5	19.0	17.0

Table XXXII

"ffect of extraction of hide prior to curing and tanning on sole leather yield* (per cent yield calculated on green wt.)

Treatment of hide	Control (Normal processing)	Experimental hides tanned directly without any beamhouse treatment	Difference in yield
Fresh hide	77.88	77.66	-0.22
Extracted with 10% Nacl Solution	78.98	81.87	+2.89
Extracted with 10% Nacl Solution + half saturated lime solution	80.08	82.54	+2.46

+ = More than control; - = Less than control

* Average of 4 samples

interfibrillary materials and fatty matters.

The general appearance of the leathers produced from experimental samples, which could not be unhaired properly, are affected considerably due to the non-uniformity and patchiness. They also appear to be somewhat hard with a tendency to crack.

Physical properties of the leathers were determined as usual and are recorded in Table XXXIII.

Apparent density and abrasion resistance do not differ between leathers produced from limed or unlimed hides. Extraction of hide prior to curing or tanning was practically no influence on these properties. No appreciable difference in tensile strength can be noted between the control and experimental leathers. The only variation in properties that may be noted is in water absorption of the leathers. Experimental leathers from unlimed hide have significantly low water absorption than the control limed samples.

6.1.2. Effect of type of cure and pretanning operations.

Samples were taken as before from freshly slaughtered hide and paired samples from both sides of the backbone were taken as control and experimental samples. Hide samples were cured in different ways (i) brining (ii) air drying (iii) dry salting and (iv) acetone dehydration. Corresponding green salted samples were always taken as control.

Brining was done by treating the hide samples in a saturated salt solution (30%) for 18 hr. at room temperature (28-30°C). After brining excess water was allowed to be drained away from the hide samples. The brined samples were kept in pile and then tanned and finished into sole leather along with the control wet salted samples.

Air drying of the samples was done in shade for a period of two days. Air dried hides were soaked for three days with the addition of Topane WS as antiseptic and Triton x 100 as wetting agent to the soak liquor. On the fourth day they were soaked in a fresh water bath

TABLE XXXIII

Effect of extraction of hide prior to curing and tanning on the physical properties* of sole leather.

Treatment of hide		Apparent density	Abrasion (inch/400 R)	Tensile strength (lb./sq.inch)	Water absorption (%) ½ hr.	Water absorption (%) 24 hr.
Fresh hide.	Control	1.259	0.099	6909	33.4	42.7
	Experimental	1.267	0.100	7254	15.8	31.9
Extracted with 10% salt solution	Control	1.268	0.122	6171	38.3	48.0
	Experimental	1.267	0.096	6554	16.3	30.0
Extracted with 10% salt solution + half saturated lime solution.	Control	1.274	0.101	5866	42.9	53.2
	Experimental	1.270	0.102	5380	24.2	32.5

* Average of two samples.

containing 0.125% H_2SO_4 and 3% salt (on volume).

In preparing dry salted hide, samples were first salted with 30% salt, piled for 3 days and then dried in the shade. They were soaked for three days in a bath containing Topane WS and Triton x 100.

Acetone dehydration was done by treating the experimental samples with increasing concentrations of acetone and then dried at room temperature. Acetone-dried samples were soaked for two days in water with the addition of Topane WS and Triton x 100. All the dry and drysalted samples were processed along with the control green salted samples.

The effect of certain pretanning operations e.g., bating and enzymic unhairing was also examined. After usual deliming the experimental samples were bated with 1% C.L.R.I. bate (No. 2) for about 4 hr. at 36°C and then washed, scudded and taken for tanning along with the control delimed samples. To prepare enzyme unhaired pelt, salted hide samples were soaked properly and then applied with 4% C.L.R.I. unhairing agent(previously mixed with 2% salt and the pH being adjusted to 8.5 with soda ash); unhairing was done after 48hr.,washed and then taken for tanning without any prior alkaline treatment. The control samples were delimed as usual and used for tanning.

The rate of increase of Ts as influenced by different curing and pretanning operations are presented in Table XXXIV.

It is apparent that the rate of tanning is practically unaffected by the different methods of cure (included in the present study). The maximum Ts has been attained in all cases after 8 days (40°Bk). Enzymic unhairing is found to have retarding influence on the rate of tanning whereas bating has no influence.

Sole leather yields of the samples those are cured by different methods and are subjected to certain pretanning operations are presented in Table XXXV.

Leather yield(calculated on green weight) appears

TABLE XXXIV

Rate of tanning (Ts °C) as influenced by various curing methods and pretanning operations.

Factors influencing rate of tanning	Delimed, bated or enzyme unhaired.	Increase in Ts (°C)						
		10° Bk (2 D)	20° BK (4 D)	30° BK (6 D)	40° BK (8 D)	60° BK (10 D)	80° Bk (12 D)	100° Bk (14 D)
Green salted (control)	0	3.5	8.5	22.5	24.0	23.0	21.0	17.5
Brined	0	3.5	8.0	22.0	23.5	22.0	20.5	18.0
Green salted (control)	0	4.0	11.0	20.5	26.5	24.0	23.5	21.5
Dry salted	0	5.0	10.0	21.5	28.0	25.5	24.5	22.0
Green salted (control)	0	4.0	12.0	21.5	24.5	23.0	21.5	20.5
Air dried	0	4.5	11.0	23.0	26.0	25.5	24.5	22.0
Green salted (control)	0	4.0	7.0	16.5	25.0	24.5	24.0	21.5
Acetone dried	0	4.5	9.0	21.0	26.5	25.5	24.5	22.5
Delimed pelt (control)	0	3.5	8.5	11.0	23.0	21.5	20.5	18.5
Bated pelt	0	3.0	8.0	11.0	23.5	21.0	19.0	17.5
Delimed pelt (control)	0	3.0	8.0	14.5	25.0	24.0	21.5	19.0
Enzyme unhaired pelt.	0	3.0	5.0	7.0	19.5	20.5	18.5	16.0

TABLE XXXV

Sole leather yield as influenced by different curing methods and pretanning operations.

Treatment	Leather yield (%) on green wt. (Average of two samples)	Variation
Green salted (control)	79.20	+ 0.93
Brined (experimental)	80.13	
Green salted (control)	81.21	+ 0.37
Dry salted	81.58	
Green salted (control)	82.20	- 0.98
Air dried	81.22	
Green salted (control)	81.76	- 0.46
Acetone dried	81.30	
Delimed (control)	78.48	+ 1.14
Bated	79.62	
Delimed (control)	77.14	- 1.13
Enzyme unhaired	76.01	

+ more than control, - less than control to be slightly reduced in case of air dried hide and enzyme unhaired pelt where as it is found to be slightly increased by brining of hide and by bating delimed plet prior to tanning. Dry salting and acetone dehydration of hide do not affect the leather yield to any great extent.

Data presented in Table XXXVI reflects the influence of different curing methods and certain pretanning operations on the physical properties of sole leathers.

It appears from the present data that abrasion, apparent density, tensile strength and water absorption are not influenced much whether the hide is curedby green salting, brining, dry salting, air drying and acetone dehydration. Bating has no effect on the physical properties whereas enzymic unhairing seems to influence the physical properties. Water absorption appears to be considerably low and apparent density and tensile strength slightly higher in leathers from enzyme unhaired pelt.

6.2. Discussion.

The present study reveals that precuring extraction of interfibrillary materials from fresh hide may expedite the rate of tannin penetration. While the diffusion of tannin is found to be incomplete in fresh hide even after 14 days' tanning, extraction of hide with 10% sodium chloride solution reduces the tanning period to 12 days for complete penetration. Extraction of hide with 10% NaCl solution + half saturated lime solution seems to have no additional influence over that of salt extraction. 10% sodium chloride solution is expected to remove most of the globular proteins from the hide which will permit some interfibrillary space for the tannins to penetrate. Removal of mucoid materials by half saturated lime is expected to provide with slightly more space in the hide but probably not significant enough to reduce further the tanning time for maximum Ts. Normal processing of the hide, however, enhances the rate of tanning and the maximum Ts has been attained by the minimum period of 10 days. Precuring extraction of the hides, processed normally, has no influence on the rate of tanning.

TABLE XXXVI

Physical properties of sole leathers as influenced by different curing methods and pretanning operations.

Treatment of hide	Physical properties *				
	Water absorption (%) ½ hr.	24 hr.	Abrasion (inch/400 R)	Apparent density	Tensile strength (lb./sq. inch)
Green salted (control)	36.8	49.7	0.090	0.825	4577
Brined	38.5	48.9	0.091	0.826	4977
Green salted (control)	43.1	50.2	0.102	0.831	6006
Dry salted	42.6	49.7	0.093	0.880	6607
Green salted (control)	41.2	46.8	0.080	0.804	6178
Air dried	42.3	47.5	0.083	0.808	5685
Green salted (control)	41.0	48.1	0.094	0.841	5047
Acetone dried	40.2	46.9	0.099	0.881	5519
Delimed ~~pelt~~ (control)	40.9	56.3	0.112	0.809	5257
Bated pelt	43.1	55.9	0.109	0.831	4933
Delimed pelt (control)	41.1	55.2	0.096	0.847	4301
Enzyme unhaired pelt	34.6	41.6	0.097	0.934	5244

* Average of two samples.

Extraction of buffalo hide with salt and with half saturated lime appears to give higher leather yield than unextracted hide. This observation is in support of the finding of Roddy[15]. In an earlier investigation Rezabek[89] observed that the leather yield in a fresh unlimed hide unhaired by the razor was much lower than the limed hide. But on the contrary to the expectation, leather yields in normally processed hides, in spite of their precuring extractions, are not higher than fresh unlimed hide samples. It may, however, be pointed out that leather yield may depend on the amount of interfibrillary materials in the hide and the extent of their removal, on the tanning procedure and the tannin materials used and so on. It is worth investigation in a bigger scale the effect of precuring sodium chloride extraction of hide or skin on the yield of vegetable tanned leather. This may have considerable practical importance.

According to Rezabek[89] fresh unlimed hide produced leather having higher tensile strength, slightly more stretch, higher wear resistance and much less water absorption.

From the present data it appears that physical properties of the leathers produced from experimental unlimed hides do not differ from that of control leather except that of water absorption, which is appreciably low in experimental leathers. Depending on the extent of tannage such a variation may be possible.

Rate of tanning (Ts) is found to be uninfluenced by different curing methods and by bating of the pelt but may be retarded to some extent in case of enzymic unhairing. The degree of rewetting of dry hide may probably be the contributing factor that may influence the rate of tanning. The slow rate of increase in Ts in enzyme unhaired sample is due to the initial high Ts of the enzyme unhaired pelt. The delay in tannin penetration in enzyme unhaired pelt may possibly be compensated by alkali treatment of enzyme unhaired pelt.

Leather yield may be slightly increased by brining, and by bating and may be slightly decreased by air drying and enzyme unhairing although the extent of variation is not very significant.

Physical properties of the leathers are not affected when the hide is cured by different curing methods. Enzyme unhairing may influence the physical properties to certain extent but bating has no such influence.

7. Summary and conclusion.

1. The effect of areawise variation in cattle hide on the changes in hydrothermal stability during pre-tanning and tanning operations was studied. The rate of chrome tanning was found to be slightly affected depending on hide structure and thickness variation. Physical properties of the finished leather were found to differ in different areas but were not always related to the thickness and structural variations. Lime splitting may possibly help in making the leather more uniform. The physical and chemical properties of the leathers did not appreciably differ whether the splitting ~~is~~ was done after liming or after tanning.

2. Buffalo hide, staled for a period upto about 24 hr. (30°C) was not appreciably deteriorated in quality but when staled for 48 hr. or more it was degraded to a considerable extent. The rate of tanning was found to be comparatively rapid in staled hides but no apparent variation was noted between staled samples.

Leather yield (weight), calculated on green weight, was not affected upto 24 hr. delay in cure. When staled for 48 hr. or more leather yield was found to be significantly reduced although this reduction in leather yield might appear to be less significant if calculated on pelt weight basis.

Apparent density of sole leather was not affected much by delay in cure. Staling of hide upto 48 hr. did not considerably influence the abrasion resistance of leather but further staling of hide resulted in higher abrasion resistance. Water absorption of leather remained unchanged upto 24 hr. staling but was increased with the increase in delay in cure.

Chemical analysis of the leathers showed that water solubles and degree of tannage might be slightly higher and hide substance slightly lower in leathers from heavily staled hides.

General appearance and assessment of the leathers were considerably affected when staled for 48 hr. or more.

3. Locational variation in buffalo hide influenced the rate of vegetable tanning as was evidenced from the rate of increase in Ts and fixed tan of pelt during tanning. The tanning period required to attain the maximum Ts varied from 6 days (30° Bk) in thinner areas to 12 days (80° Bk) in thicker areas. Rate of tanning fixation varied moderately during early stages of tanning but the variation was less distinct at later stages of tanning. Thickness variation in hide was found to have good correlation with the rate of tanning.

Leather yields, both in weight and area, were found to vary in different locations of the hides. Both thickness and structural variation in hide may be involved in such variations.

Certain physical properties of the leathers were found to vary in different locations of the buffalo hide. Water absorption and tensile strength was found to vary depending on the areawise variation in hide but apparent density of the leather was practically unaffected. Apparent density of the acetone dried delimed pelt appeared to have no direct correlation with the apparent density of finished leather. Abrasion resistance might vary in different areas of the leather but no regular trend of variation was noted in the present study. These variations in physical properties are probably caused by both thickness and structural variations throughout the side.

When the side was divided into three segments (A - adjacent to backbone, B - Central, C - adjacent to belly and shanks) in parallel to the line of backbone and the segments were compared for leather yield and other properties it appeared that the sole leather making potentiality of buffalo hide decreased in the following order B > A > C. The rate of tanning, however, increased in the same order.

4. Rate of tanning was found to be enhanced by extracting the hide with salt and half saturated lime solution. Liming and deliming of the hide further increased the rate of tanning.

Extraction of interfibrillary materials from fresh hide by salt and lime solution was found to increase the leather yield. But it was striking to note that leather yields in unlimed experimental hides were not less than the control limed hides.

Except water absorption, which was found to be higher in control limed hides, other physical properties of the leathers were not affected much by the precuring and pretanning extractions of hide.

Leather from unlimed hides were somewhat hard and had the tendency to crack in the grain. Different curing methods seemed to have no influence on the rate of tanning provided they were soaked back properly before processing. Bating did not help expediting tannin penetration to any considerable extent whereas enzyme unhairing retarded the rate of tanning.

Leather yield might possibly be influenced by curing methods (e.g. brining and airdrying) and pre-tanning operations (e.g. bating and enzyme unhairing) but not very significantly.

CHAPTER IV

1. Leather making potentiality of cattle hides obtained from fallen (dead) and slaughtered animals and cured by different methods

2. Methods

2.1 Assessment of raw hides

2.1.1 Visual assessment

Visual assessment of the hides was made on the basis of (a) general appearance (b) flay cuts and holes (c) substance (d) flankiness (e) sores, scratches and other grain damages and (f) curing defects e.g. hair-slip and red-heat. Hides were graded into four categories i.e. first, second, third and rejection quality.

2.1.2 Histological assessment

A sample from each hide was taken from identical positions, washed well with water and then fixed in formol saline. Hide sections were cut by a freezing microtome, stained with different staining agents and then examined in a microscope for the following:

(a) adherence of epidermis to corium
(b) cells of grain layer
(c) compactness of the fibre structure
(d) thickness of the fibres
(e) substance (thickness of the hide)
(f) extent of bacterial penetration

A maximum of 8 points and a minimum of 2 points were given to each item and the average of these values was considered as indicative of the quality of the hide. Histologically also the hides were classified into four categories: Very poor, poor, fair and good.

2.1.3 Physical properties of raw hides

Samples were taken from the butt area of the hide in a direction perpendicular to the back bone (Fig.1), fleshed and washed and dehydrated in increasing concentrations of acetone for a period of 4 - 5 days. Tensile strength and elongation of the acetone dried hide samples were determined[62] in a Scott testing machine.

2.1.4 Chemical analysis

Samples taken from each hide were cut into small squares (5 mm. side). 10 g. of the samples was taken for moisture determination and 5 g. of the samples for fat estimation. Moisture was determined by the ALCA method[90]. During fat determination, the hide samples were first hydrolysed with 6N HCl and then extracted with chloroform[91]. Ash was determined by heating 5 g. hide samples in a muffle furnace at about 700°C. For hydroxyproline estimation, hide pieces were unhaired with a safety razor and the adhering flesh layer was removed. They were washed well with distilled water to free them from salt and then dehydrated with acetone. Newman and Logan method was followed in estimating hydroxyproline.

2.2 Assessment of leather quality

All the hides were tanned and finished into chrome tanned shoe upper leather. They were taken in a number of experimental lots with both the slaughtered and fallen hides in each lot.

The efficiency of tanning of the hides was adjudged from visual assessment of the quality of the leather, physical properties and chemical properties of the leathers. Visual assessment and physical properties of the leathers were determined according to the procedures mentioned in Chapter I. Chemical analyses of the leathers e.g. moisture, hide substance, Cr_2O_3 and fat were carried out according to standard procedures.

2.3 Statistical analysis of the physical properties

To summarise the physical properties of the hides and leathers and to compare them between the slaughtered and fallen hides and shoe upper leathers produced from them statistical method of analysis was followed. Different statistical values were calculated according to the formulae given below:

Standard deviation (s.d.) $= \sqrt{\dfrac{\Sigma(x-\bar{x})^2}{n}}$

where x - actual value

$\bar{x}$ - mean value

n - number of samples

Co-efficient of variation (c.v.) = $\dfrac{sd \times 100}{\bar{x}}$

d - value $\dfrac{\bar{x}_S - \bar{x}_F}{\dfrac{(Sd_S)^2}{n_S} + \dfrac{(Sd_F)^2}{n_F}}$

where $\bar{x}_S$ - mean for slaughtered hides

$\bar{x}_F$ - mean for fallen hides

Sd_S - Standard deviation for slaughtered hides

Sd_F - Standard deviation for fallen hides

n_S - Number of slaughtered hides

n_F - Number of fallen hides

3. Comparative study of the leather making properties of fallen hides obtained from Flaying and Carcass Utilisation Centres and slaughtered hides obtained from slaughter houses

3.1. Experimental procedure and results

Thirty two fallen cattle hides were obtained at random from the Flaying and Carcass Utilization Centres near Bombay and Calcutta and thirty six slaughtered cattle hides were collected from slaughter houses in Bombay and Calcutta. It may, however, be mentioned that in Indian slaughter houses, young cattle, particularly cows, are not slaughtered. In Bombay Flaying and Carcass Utilization Centre, all the fallen hides could not be collected at a time due to non-availability; the hides were thus salted and stored in the centre for considerably a longer period before they were processed. The slaughtered and fallen hides were visually examined after they were received.

The qualities of the slaughtered and fallen hides as assessed by visual inspection are reported in Fig.14.

Bombay slaughtered hides had no adhering fat and were clean, well cured but mechanical damages like scratches and abrasion on the hair side affected the hides. The fallen hides were of poor quality showing easy hair slip and suffered from considerable grain damage. Fallen hides were also partially dried out.

Calcutta slaughtered hides were clean, well cured, had no excess flesh, but were damaged due to flay cuts. Many of the fallen hides showed slight hair slip and retained slightly more adhering flesh. Both the slaughtered and fallen hides possessed large flank areas.

It is evident from Fig.14 that the fallen hides collected from the Flaying and Carcass Utilization Centres are poor in quality compared to slaughtered hides.

Histological assessment values of the slaughtered and fallen hides are given in Table XXXVII. According to histological assessment, 24 slaughtered hides are classified as good and 12 as fair. The classification of the fallen hides are as follows:

Good - 9
Fair - 11
Poor - 12

The tensile strength and elongation at break of the acetone dried hides are given in Table XXXVIII.

Tensile strength and elongation data do not give much indication about the quality of the individual hides. On an average, the tensile strength of the slaughtered hides seems to be higher than that of the fallen hides and this is more prominent in Calcutta hides. Percent elongation, on the other hand, appears to be lower in slaughtered hides. Average strength-elongation products do not differ much in Bombay slaughtered and fallen hides but in Calcutta hides, the strength-elongation product is appreciably higher in the case of slaughtered hides.

Data on chemical analysis of the hides are presented in Table XXXIX.

TABLE XXXVII

Histological assessment of slaughtered and fallen hides

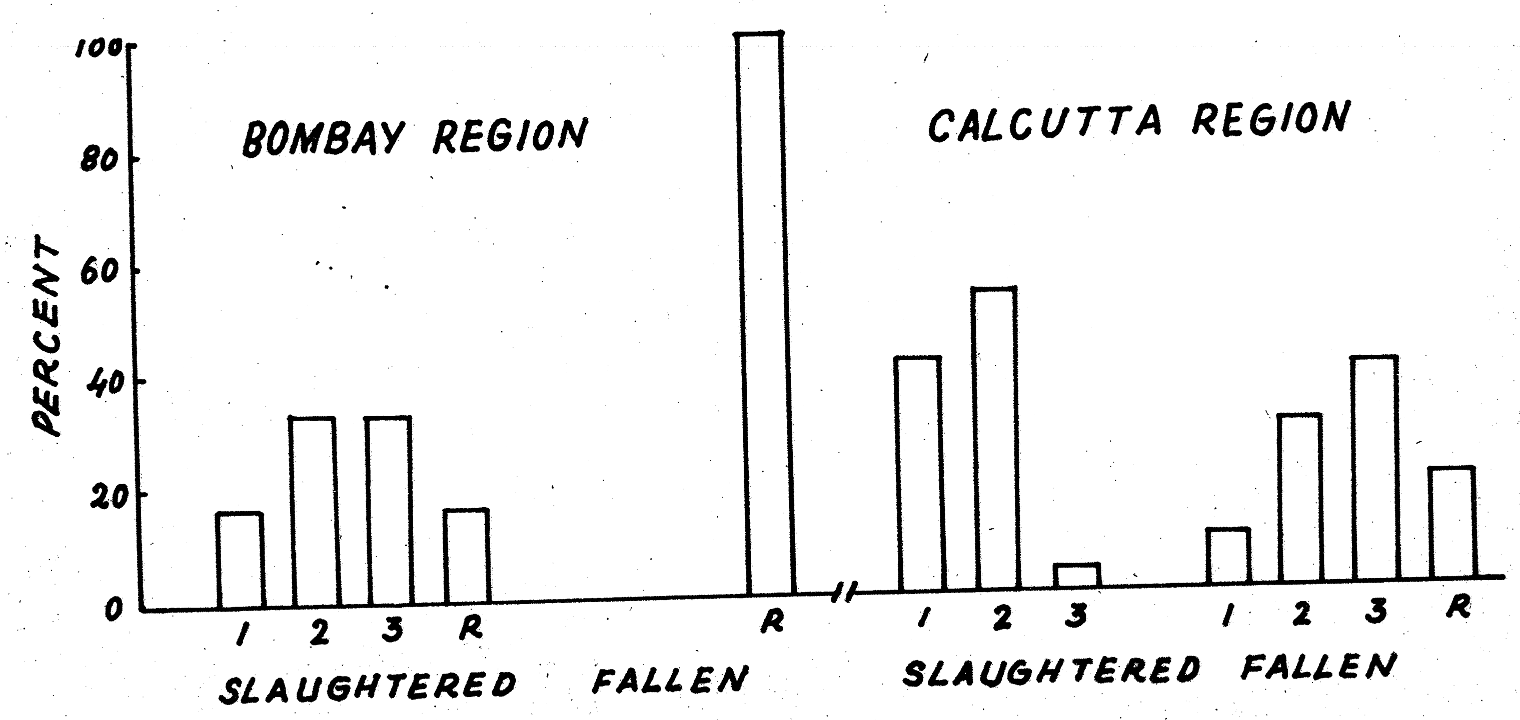
Assessment	No. of hides	
	Slaughtered	Fallen
BOMBAY REGION		
Good	9	-
Fair	3	4
Poor	-	8
Very Poor	-	-
CALCUTTA REGION		
Good	15	9
Fair	9	7
Poor	-	4
Very Poor	-	-

TABLE XXXVIII

Physical properties of acetone dried slaughtered and fallen hides

Physical roperties	Slaughtered hides			Fallen hides		
	Maximum	Minimum	Average	Maximum	Minimum	Average
MBAY REGION						
ensile trength lb/sq. inch)	6901	4423	5908	6901	4054	5429
longation (%)	60	44	54	86	45	60.5
trength-longation roduct	401640	238842	317487	430430	227024	327357
LCUTTA REGION						
ensile trength lb./sq. inch)	8991	4098	6794	6530	3053	4892
longation (%)	81	27	55	82.5	40	58
trength-longation roduct	541080	110646	376888	458475	145692	277780

FIG : 14



BOMBAY REGION
CALCUTTA REGION
PERCENT
100
80
60
40
20
0
1
2
3
R
SLAUGHTERED
R
FALLEN
1
2
3
SLAUGHTERED
1
2
3
R
FALLEN

TABLE XXXIX

Chemical analysis of slaughtered and fallen hides

Chemical analysis	Slaughtered hides			Fallen hides		
	Maximum	Minimum	Average	Maximum	Minimum	Average
BOMBAY REGION						
Moisture (%)	45.04	40.41	43.87	41.40	32.78	36.35
Ash (%)	16.97	12.84	14.58	16.27	10.34	13.27
Fat (%)	8.46	4.66	6.13	9.46	2.80	5.22
Hydroxyproline (% on salt & moisture free wt.)	11.63	10.20	10.73	11.99	9.75	10.42
CALCUTTA REGION						
Moisture (%)	44.22	38.51	42.0	47.0	31.63	39.28
Ash (%)	16.34	12.25	14.68	18.99	13.31	15.19
Fat (%)	7.02	3.01	5.70	6.99	3.27	5.40
Hydroxyproline (% on salt & moisture free wt.)	12.80	9.73	11.40	12.30	9.40	10.60

Moisture and ash content of all the slaughtered hides and Calcutta fallen hides appear to be within the range of normal well cured hides. Bombay fallen hides are dried up to some extent and the salt content(ash) in some of the hides is quite low. Fat and hydroxyproline content in slaughtered and fallen hides, on an average, do not vary to any great extent.

Observations during processing

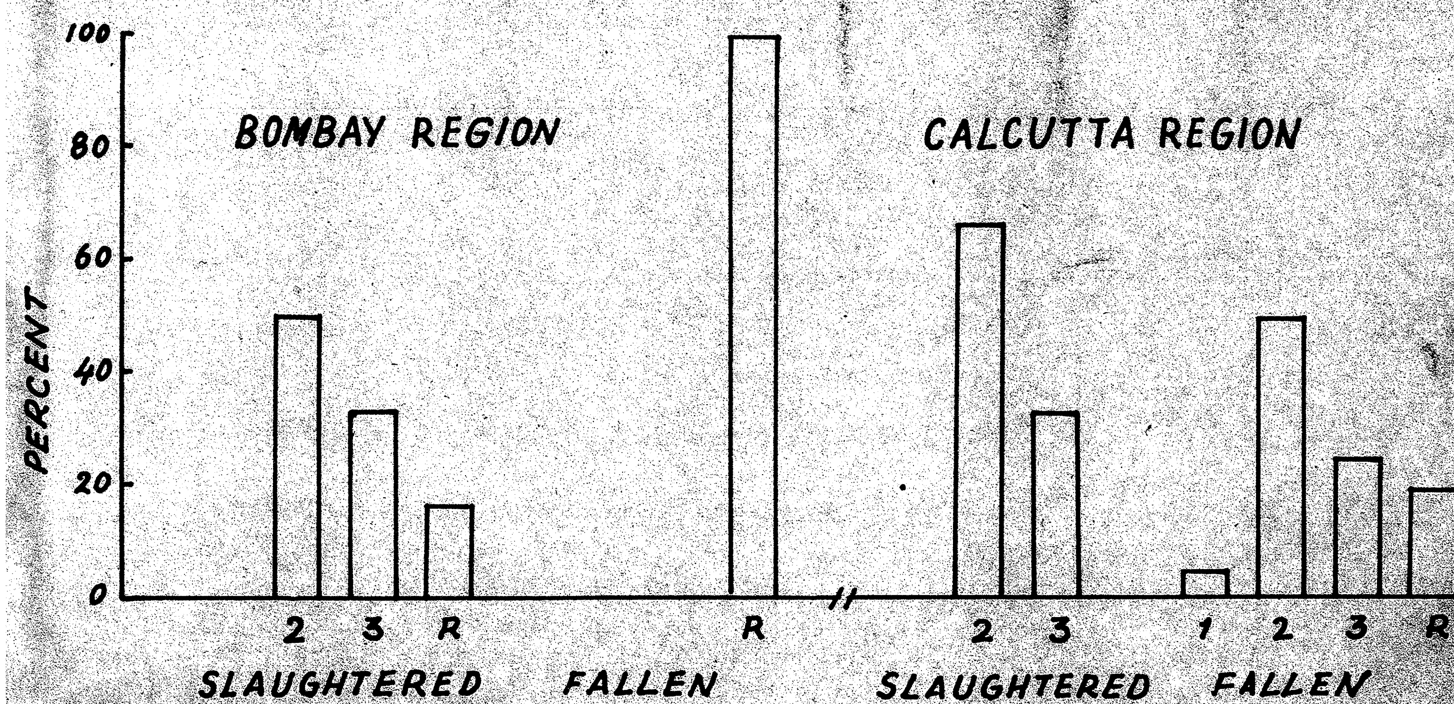
After liming, it was noted that most of the fallen hides from Bombay area were severely degraded with considerable grain damage. Of these four heavily damaged hides could not be finished into upper leathers. It was, however, noted during blue selection that only 53% of the slaughtered hides and about 31% of the fallen hides were suitable for finishing into full chrome shoe upper leathers.

Visual assessment of the quality of finished leathers is presented in Fig.15.

It is noteworthy that out of 36 slaughtered hides no single piece was graded into first quality, 22 pieces were graded as seconds, 12 pieces as thirds and 2 pieces as rejections. The quality of the leathers from Bombay slaughtered hides is found to be affected due to coarser break, lack of suppleness and presence of vein marks. Two hides yielded rejection quality leathers because of poor substance, and scar, tick and vein marks. Slaughtered hides from Calcutta region were found to be degraded in quality due to deep flay cuts, tick and vein marks. Leathers from both the slaughtered and fallen hides of this region had more flank areas.

All the fallen hides from Bombay region produced rejection quality leathers. Some of these leathers were otherwise good except for severe grain damage (Fig.16). Such grain damages could possibly be avoided by minimising the delay in cure and following more effective curing. Fallen hides from Calcutta region were much better than Bombay fallen hides. These leathers were free from severe grain damages and flay cuts but were deteriorated in quality due to such defects as tick marks, blisters and poor flanks. Out of 32 pieces of leathers from fallen

FIG: 15


PERCENT
100
80
60
40
20
0
BOMBAY REGION
CALCUTTA REGION
2
3
R
R
2
3
1
2
3
R
SLAUGHTERED
FALLEN
SLAUGHTERED
FALLEN

hides, one piece was graded as first quality, 10 pieces as seconds, 5 pieces as thirds and 16 pieces as rejection quality. Finished leather selection thus supports the previous observation that fallen hides collected from Flaying and Carcass Utilization Centres are comparatively poorer in quality than the slaughtered hides for making full chrome shoe upper leathers.

The physical properties of the leathers from slaughtered and fallen hides are presented in Table XXXX.

Physical properties of most of the leathers from slaughtered and fallen hides may be considered as acceptable for normal quality chrome upper leather. Certain leathers from both slaughtered and fallen variety, have lower values for tensile strength, grain crackiness and bursting strength. Here again, it may be noted that the tensile strength values of the leathers from fallen hides are comparatively lower and the elongation values higher than those for the leathers from slaughtered hides although the difference is very little in case of Calcutta hides. In leathers from Bombay region, the strength at grain crack and bursting strength are slightly less in fallen hides but they do not vary much in leathers from Calcutta hides.

The chemical analysis of the leathers both from slaughtered and fallen hides is given in Table XXXXI.

The chemical composition of the leathers from slaughtered and fallen hides does not differ significantly except that the fat content of the leathers from Bombay fallen hides is slightly higher than that of leathers from Bombay slaughtered hides. This may be due to considerable grain damage in the hides caused by bacterial action which has facilitated more fat uptake.

Statistical analysis of tensile strength and elongation of acetone dried hide is given in Table XXXXII and of physical properties of finished leathers in Table XXXXIII.

3.2. Discussion

In the present investigation the assessment of the quality of raw hide in order to find out its leather making potentiality has been made by examining the hides

TABLE XXXX

Physical properties of leathers made from slaughtered and fallen hides.

Physical properties		Slaughtered hides			Fallen hides		
		Maximum	Minimum	Average	Maiximum	Minimum	Average
BOMBAY REGION							
Tensile strength	⊥	5928	2846	4193	3998	2629	3123
(lb./sq. inch)	=	4249	1954	3067	4176	1463	2766
Elongation (%)	⊥	51.0	37.5	45.0	86.0	47.5	63.0
	=	51.0	35.0	43.0	62.5	41.0	50.0
Stitch tear strength	⊥	1456	1016	1303	1170	970	1112
(lb./inch)	=	1492	1016	1216	1310	910	1109
Tongue tear strength	⊥	307	176	242	296	176	233
(lb./inch)	=	343	189	278	346	191	243
Grain crack strength (lb./sq. inch/inch)		15663	4638	11149	12505	3712	6501
Bursting strength (lb./sq.inch/inch)		19538	4638	13741	16595	6531	10201
Strength-elongation-product	⊥	287508	106725	189102	309845	147750	200445
(lb.sq. inch)	=	211497	80505	133651	189200	68127	135439
CALCUTTA REGION							
Tensile strength	⊥	4622	2337	3588	4640	1870	3336
(lb./sq. inch)	=	4580	2337	3366	4585	1963	3130
Elongation (%)	⊥	75	37	51	77	31	54
	=	59	37	46	56	34	43
Stitch tear strength	⊥	1714	1143	1420	1613	867	1362
(lb./inch)	=	1664	864	1317	1478	775	1255
Tongue tear strength		508	226	399	470	242	338
(lb./inch)		508	216	300	475	173	300
Grain crack strength (lb./sq. inch/inch)		15702	5362	9916	22000	11618	11157
Bursting strength (lb./sq.inch/inch)		21844	16160	14639	22000	8313	13550
Strength-elongation-product	⊥	264825	14160	185117	278922	57970	180939
(lb./sq.inch)	=	270220	102878	157349	194876	68102	132034

TABLE XXXXI

Chemical analysis of finished leathers produced from slaughtered and fallen hides

Chemical analysis	Slaughtered hides			Fallen hides		
	Maximum	Minimum	Average	Maximum	Minimum	Average
BOMBAY REGION						
Moisture (%)	12.57	11.27	11.9	12.97	11.33	12.04
Cr_2O_3 (%)	3.91	3.61	3.75	3.99	3.70	3.66
Fat (%)	4.65	3.34	3.84	4.51	3.66	4.10
Hide substance (%)	65.32	63.53	64.74	64.85	63.26	64.54
CALCUTTA REGION						
Moisture (%)	15.83	13.77	14.43	15.48	13.99	14.59
Cr_2O_3 (%)	4.19	3.50	4.10	4.26	3.97	4.11
Fat (%)	4.34	3.50	3.92	4.41	3.28	3.88
Hide substance (%)	65.89	62.02	64.87	65.46	63.03	64.23

Table XXXXII

Statistical analysis of the physical properties of raw hides collected from slaughter houses and Flaying and Carcass Utilisation Centres

Physical properties	Slaughtered				Fallen				
	No.of samples	Mean	s.d.	c.v.	No.of samples	Mean	s.d.	c.v.	d-value
Tensile strength ⊥ (lb/sq. inch)	32	6674	1007	15.1	32	5027	905	18.0	6.9*
Elongation ⊥ (%)	"	55	9.8	17.8	"	5.9	12.5	21.2	0.45

* Significant

Table XXXXIII

Statistical analysis of the physical properties of leathers from slaughtered hides collected from slaughter houses and fallen hides collected from Flaying and Carcass Utilisation Centres

Physical properties		Slaughtered				Fallen				
		No.of samples	Mean	s.d.	c.v.	No.of samples	Mean	s.d.	c.v.	d-value
Tensile strength (lb/sq.in)	∥	28	3418	597	16.9	28	3000	799.1	26.6	2.3*
	⊥	"	3862	694	18.0	"	3271	691.1	21.6	3.2*
Elongation (%)	∥	"	45	4.75	10.6	"	44.5	6.4	14.4	0.34
	⊥	"	46.5	5.2	11.2	"	56.0	10.5	18.7	4.25*
Stitch tear strength (lb/inch)	∥	"	1294	185.8	14.3	"	1212	204.3	16.8	1.6
	⊥	"	1411	176.2	12.5	"	1271	194.1	15.3	2.8*
Tongue tear strength (lb/inch)	∥	"	317	57.7	18.2	"	283	77.2	27.2	1.9
	⊥	"	308	78.1	25.3	"	308	76.7	24.9	0
Grain cracking strength		"	10582	2896	27.4	"	9760	4610	47.2	0.86
(lb/sq.inch/ inch)		"								
Bursting strength (lb/sq.inch/ inch)		"	14329	2406	16.8	"	12591	3657	29.0	2.1*

* Significant

visually, histologically and by determining some physical and chemical characteristics.

According to visual assessment, the slaughtered hides are classified into the following grades:

1st quality - 33.33%, 2nd quality - 47.22%, 3rd quality - 13.89% and rejection - 5.56%;

the fallen hides are graded as:

1st quality - 6.25%, 2nd quality - 18.75%, 3rd quality - 25.0% and rejection 50%. It is thus apparent that slaughtered hides obtained from slaughter houses are, on the average, better raw materials than fallen hides available in Flaying and Carcass Utilization Centres. It is however, worthy of note that only one third of the slaughtered hides is graded into 1st quality and some of them are even considered as rejections. Two factors mainly responsible for the devaluation of the slaughtered hides are flaying defects and restrictions on cattle slaughter; mostly aged animals are slaughtered in slaughter houses and the hides are generally damaged by parasites, diseases and sores.

Fallen hides are found to be appreciably free from flaying defects but are degraded due to damages caused by delay in flaying and curing, improper cure and careless handling. Fallen hides obtained from Bombay region are severely damaged in the grain probably due to these reasons.

Like visual assessment, histological assessment also reveals that, in general, the slaughtered hides are superior in quality to the fallen hides.

Table XXXIX shows that the average tensile strength of the slaughtered hides is slightly higher and average elongation slightly lower than that of fallen hides. The strength elongation product gives the work done to break the sample. The average strength elongation product seems to be slightly higher in acetone dried samples of slaughtered hides but practically no difference is noted between finished leathers produced from slaughtered and fallen hides.

Chemical analysis of the hides does not give much indication about the quality of individual hides. In a properly cured hide the moisture present is to be saturated with salt. Although most of the slaughtered and fallen hides satisfy this criterion of a good cured hide, some fallen hides obtained from Bombay are cured probably with inadequate quantities of salt and thus subjected to severe deterioration in quality during storage. Hydroxyproline content of the fallen hides on an average, appears to be slightly less than that of slaughtered hides.

It appears that the physical properties of the hides have no relation to the assessment of quality as practised by the trade. This is because the present method of assessment is based on visual observation of defects which are only found at certain points on the hides whereas physical properties are determined on samples taken from the prescribed regions, which may be devoid of such defects. A real deterioration in the whole of the hide would certainly show up in the strength and elongation properties whereas a hide without visible defects need not necessarily yield a good leather.

This is confirmed by the fact that although 12 slaughtered hides have been classed into 1st quality by visual inspection, none of them has turned out as 1st quality after finishing into full chrome upper. Considerable damage due to flay cuts, pock and tick marks, prominent vein marks and other defects that remained unidentified during visual inspection is mainly responsible for such degradation of leather quality.

An example of how hide quality is tied up with physical praperties is shown by the lower tensile strength and higher elongation of fallen hides as compared to slaughtered hides of the Bombay region which point to a higher degree of deterioration of fallen hides and this is reflected in the leathers made from these two varieties of hides, the tensile strength being lower and the elongation at break being higher in the fallen hides. These observations on the physical properties are in conformity with the observation that the fallen hides of the Bombay region were not cured or preserved as well as the slaughtered hides.

In case of the hides of the Calcutta region, the differences in the tensile strength and elongation values are not as much as in the Bombay region and this could be attributed to the better curing of the fallen hides effected in the Calcutta region. Similar observations hold good for the other physical properties.

After a critical study of the leathers obtained from slaughtered hides, it was noted that 2 pieces are upgraded and 20 pieces degraded, the rest being of the same quality as that of raw selection. In case of fallen hides, 5 pieces are found to be upgraded after finishing, 4 pieces are degraded in quality and the rest 23 pieces follow the same raw assessment. This shows that the leather making potentiality of fallen hides remains unaffected provided the condition of the raw hide is found acceptable for its quality comparable to slaughtered hides.

Though the limitations of the assessment values for different grades of hides have been arbitrarily chosen, the histological assessment of the raw hides appears to be moderately comparable to the finished leather selection. Six pieces of leathers from slaughtered hides are found to be upgraded, 9 pieces are rated as lower grades and 21 pieces are graded into the same raw selections. On the other hand 7 pieces of leather from fallen hides are upgraded, 12 pieces degraded and 23 pieces follow the raw selection. It may also be mentioned that 4 fallen hides from Bombay region that are found severely damaged and unsuitable for finish have very low assessment values.

No appreciable difference can be seen between leathers from slaughtered and fallen hides in respect of other physical properties. Chemical analysis of the leathers do not indicate any difference between the qualities of the leathers from fallen and slaughtered hides.

Statistical analysis of the data on tensile strength and elongation of acetone dried hides show that (Table XXXXII) difference value in tensile strength (perpendicular) is significant in favour of slaughtered hides but is insignificant for elongation. Both in the cases of tensile strength and elongation the co-efficient of variation is, however, higher in fallen hides.

It appears from Table XXXXIII that the difference values for tensile strength, elongation (perpendicular), stitch tear strength (perpendicular) and bursting strength is significant in favour of slaughtered hides whereas the difference values are insignificant for tongue tear strength and grain cracking strength. Except for tongue tear strength (perpendicular), coefficient of variation is found to be higher in fallen hides for all other properties.

4. Comparative study of the leather making properties of fallen and slaughtered hides obtained from hide markets

4.1. Experimental procedure and results

Twelve slaughtered and twelve fallen cattle hides were collected from hide markets in Agra, Meerut and Jullundur in Northern India; twenty four slaughtered and twenty four fallen hides were obtained from raw hide dealers in Coimbatore, Bangalore and Ernakulam in Southern India.

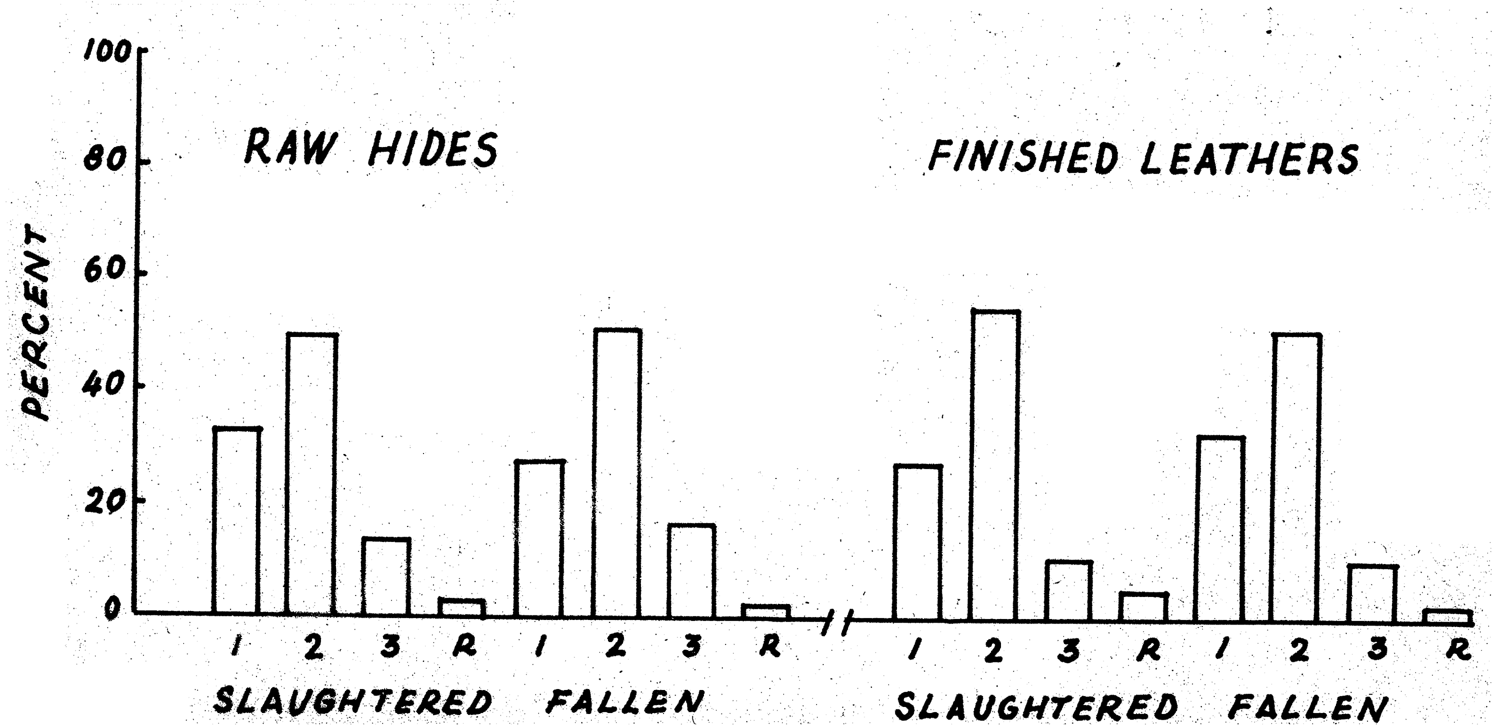
Visual assessment of the quality of slaughtered and fallen hides is given in Table XXXXIV. The qualities of slaughtered and fallen hides collected from different places in Northern and Southern India, as assessed by visual inspection, are comparable to each other without any great variation. The average classification of the total number of hides collected from both the Northern and Southern regions is presented in Fig.47.

Classification of the hides as assessed by histological study is given in Table XXXXV. This again shows that there is practically no variation in quality between the market quality slaughtered and fallen hides.

Tensile strength and elongation of the acetone dried hides are given in Table XXXXVI. The tensile strength of market quality fallen hides appear to be comparable to that of market quality slaughtered hides. Percent elongation, however, seems to be higher in fallen hides than in slaughtered hides. On the other hand, strength-elongation product is found to be higher in fallen hides from Northern and Southern regions.

The data on chemical analysis of the slaughtered and fallen hides are presented in Table XXXXVII which show

FIG: 17



PERCENT
100
80
60
40
20
0
RAW HIDES
FINISHED LEATHERS
1 2 3 R 1 2 3 R
SLAUGHTERED FALLEN
1 2 3 R 1 2 3 R
SLAUGHTERED FALLEN

Table XXXXIV

Visual assessment of market quality slaughtered and fallen hides

Quality	Slaughtered	Fallen
	%	
NORTHERN REGION (12 hides)		
First	33.33	16.67
Second	58.33	58.33
Third	8.33	25.00
Rejection	Nil	Nil
SOUTHERN REGION (24 hides)		
First	33.33	33.33
Second	45.83	50.00
Third	16.67	12.50
Rejection	4.17	4.17

Table XXXXV

Histological assessment of market quality slaughtered and fallen hides

Quality	Slaughtered	Fallen
	%	
NORTHERN REGION (12 hides)		
Good	50.0	50.0
Fair	41.67	41.67
Poor	8.33	8.33
Very poor	Nil	Nil
SOUTHERN REGION (24 hides)		
Good	25.0	25.0
Fair	70.83	70.83
Poor	4.17	4.17
Very poor	Nil	Nil

Table XXXXVI

Physical properties of acetone dried hides

Type of raw hides		Tensile strength (lb./sq. inch)	Elongation (%)	Strength-elongation product (lb./sq. inch)
NORTHERN REGION				
Slaughtered hides	Maximum	10530	62.5	326453
	Minimum	3463	31.0	159320
	Average of 12 hides	5508	45.0	237723
Fallen hides	Maximum	9151	55.0	404130
	Minimum	4948	35.0	173180
	Average of 12 hides	7446	48.0	326844
SOUTHERN REGION				
Slaughtered hides	Maximum	6697	75.0	461127
	Minimum	3729	40.0	227295
	Average of 24 hides	5479	62.0	335266
Fallen hides	Maximum	7042	84.0	510545
	Minimum	4451	40.0	285562
	Average of 24 hides	5420	68.0	371937

Table XXXXVII

Chemical composition of market quality slaughtered and fallen hides

Type of raw hides		Moisture %	Ash %	Fat %	Hydroxyproline %
NORTHERN REGION					
Slaughtered hides	Maximum	44.0	18.3	8.0	13.0
	Minimum	31.2	15.5	2.32	11.5
	Average of 12 hides	40.0	17.3	5.37	12.3
Fallen hides	Maximum	42.4	18.2	9.73	13.5
	Minimum	36.0	13.0	3.41	11.0
	Average of 12 hides	39.8	16.4	5.70	12.3
SOUTHERN REGION					
Slaughtered hides	Maximum	42.0	18.1	4.86	12.0
	Minimum	36.0	13.4	3.02	10.0
	Average of 24 hides	40.0	15.2	3.80	11.0
Fallen hides	Maximum	44.0	17.8	4.65	12.0
	Minimum	35.0	13.4	3.0	9.0
	Average of 24 hides	39.0	15.5	3.80	10.5

that chemical composition of the fallen hides collected from different hide markets does not vary to any appreciable extent from that of market quality slaughtered hides. This is quite probable in view of the fact that the fallen hides that are generally brought to the hide market are collected in time, cured in a better way and resalted if necessary.

Visual assessment of the leathers are presented in Table XXXXVIII.

It is apparent from Table XXXXVIII that the qualities of finished leathers obtained from market quality fallen hides of both the northern and southern regions are very well comparable to those of market quality slaughtered hides. Average classification of the qualities of total number of leathers from slaughtered and fallen hides is depicted in Fig.17.

The physical properties of the leathers made from slaughtered and fallen hides are given in Table XXXXIX.

Though there may be considerable variations between the maximum and minimum values both in case of slaughtered and fallen hides, the average values for tensile strength, elongation, stitch tear strength, tongue tear strength, grain cracking strength and bursting strength of leathers obtained from market quality fallen hides do not differ to any considerable extent from the corresponding average values of leathers from market quality slaughtered hides. Average values for strength-elongation product also appear to be close to each other.

Table L comprises with the data on chemical analysis of the leathers produced from slaughtered and fallen hides. Chemical composition of the leathers appears to be practically identical irrespective of the slaughtered and fallen variety of the hides.

Statistical analyses of tensile strength and elongation of acetone dried hide is given in Table LI and of physical properties of finished leathers is given in Table LII.

A summarisation of statistical analysis data on physical properties of total no. (T.3.+4 of Ch.IV) of hides and leathers is presented in Tables LIII and LIV.

Table XXXXVIII

Visual assessment of the quality
of finished leathers

Type of raw hides	Slaughtered	Fallen
NORTHERN REGION (12 hides)		
First	33.33	33.33
Second	50.00	58.33
Third	16.67	8.33
Rejection	Nil	Nil
SOUTHERN REGION (24 hides)		
First	25.0	33.33
Second	58.33	50.0
Third	8.33	12.50
Rejection	8.33	4.17

Table XXXXIX

Physical properties of finished leathers from market quality slaughtered and fallen hides

Type of raw hides		Tensile strength (lb/sq.inch)		Elongation (%)		Stitch tear strength (lb/inch)		Tongue tear strength (lb./inch)		Grain cracking strength (lb/inch)	Bursting strength (lb./sq. inch)	Strength elongation product ( ) (lb/sq.inch)	
		⊥	∥	⊥	∥	⊥	∥	⊥	∥			⊥	∥
NORTHERN REGION													
Slaughtered	Max.	7297	6119	60.0	59.0	2014	1913	521	469	23207	25000	364850	253624
	Min.	2118	2437	27.5	34.0	857	780	190	222	4826	6096	65092	82994
	Average	4260	3885	48.0	44.5	1563	1401	378	345	10463	13604	206376	180934
Fallen	Max.	6472	6543	64.0	62.5	2117	1934	508	535	19878	23466	362125	310792
	Min.	2380	1805	32.5	27.5	1080	1048	240	209	6209	7620	88758	49637
	Average	4117	4184	51.0	44.0	1487	1432	375	361	10817	14992	212589	190644
SOUTHERN REGION													
Slaughtered	Max.	6321	6592	65.5	55.0	1915	1882	531	508	18288	18473	380751	355988
	Min.	3225	2726	40.0	37.5	1295	974	319	305	4620	11006	129000	119944
	Average	1682	4052	55.0	47.0	1613	1398	414	375	9366	15560	261491	190871
Fallen	Max.	3591	6491	72.0	55.0	1916	1974	533	466	17780	20956	346808	357005
	Min.	2782	2354	40.0	36.0	1088	986	264	254	4670	9698	139100	103576
	Average	4535	3930	54.0	46.0	1516	1518	378	340	10067	15032	243145	187292

Table L

Chemical analysis of the finished leathers from market quality slaughtered and fallen hides

Type of raw hides		Moisture	Cr_2O_3	Fat	Hide substance
			%		
NORTHERN REGION					
Slaughtered	Maximum	12.57	3.91	4.65	65.32
	Minimum	11.27	3.61	3.34	63.53
	Average	11.92	3.75	3.84	64.74
Fallen	Maximum	12.97	3.99	4.51	64.85
	Minimum	11.33	3.70	3.66	63.26
	Average	12.04	3.84	4.10	64.54
SOUTHERN REGION					
Slaughtered	Maximum	17.0	4.55	4.55	65.5
	Minimum	13.0	3.84	3.25	64.0
	Average	15.0	4.20	3.95	64.5
Fallen	Maximum	17.0	4.55	4.22	65.0
	Minimum	13.5	3.25	3.22	63.0
	Average	15.0	4.08	3.78	64.5

TABLE LI

Statistical analysis of the physical properties of market quality slaughtered and fallen hides.

Physical properties	Slaughtered				Fallen				d-value
	No. of samples	Mean	s.d.	c.v.	No. of samples	Mean	s.d.	c.v.	
Tensile strength ⊥ (lb./sq.inch)	36	5488	1341	24.4	36	6040	1274	21.1	1.79
Elongation(%) ⊥	"	56.5	13.8	24.4	"	60	15.1	24.9	1.1

TABLE LII

Statistical analysis of the physical properties of leathers from market quality slaughtered and fallen hides.

Physical properties		Slaughtered				Fallen				d-value
		No. of samples	Mean	s.d.	c.v.	No. of samples	Mean	s.d.	c.v.	
Tensile strength (lb./sq. inch)	||	36	3856	950	19.8	36	3900	1102	22.9	0.21
	⊥		4301	1200	27.9		4504	1179	26.1	0.26
Elongation (%)	||	"	50.0	8.4	16.6	"	46.0	6.1	13.2	2.7*
	⊥		51.0	7.5	14.7		52.5	8.1	15.4	1.1
Stitch tear strength (lb./inch)	||	"	1410	317.0	22.5	"	1537	285.0	18.5	2.1*
	⊥		1535	242.3	15.8		1571	238.7	15.2	0.72
Tongue tear strength (lb./inch)	||	"	379	68.3	18.0	"	364	82.5	22.7	1.0
	⊥		384	79.5	20.7		381	67.4	17.6	0.2
Grain cracking strength (lb./sq.inch/inch)		"	10078	3943	39.1	"	10833	4310	39.7	0.89
Burshing strength (lb/sq.inch/inch)		"	14167	3588	24.6	"	15307	3243	21.2	1.6

* Significant

TABLE LIII

Statistical analysis of the physical properties of total number of raw slaughtered and fallen hides.

Physical properties		Slaughtered				Fallen				d-value
		No. of samples	Mean	s.d.	c.v.	No. of samples	Mean	s.d.	c.v.	
Tensile strength (lb./sq. inch)	⊥	84	5993	456.7	7.62	76	5571	384.0	6.9	4.08
Elongation(%)	⊥	"	55.5	12.6	22.8	"	60	14.2	23.7	0.64

TABLE LIV

Statistical analysis of the physical properties of leathers obtained from total number of slaughtered and fallen hides.

Physical properties		Slaughtered				Fallen				d-value
		No. of samples	Mean	s.d.	c.v.	No. of samples	Mean	s.d.	c.v.	
Tensile strength	∥	84	3639	698.2	19.2	76	3625	1245	34.3	0.96
(lb./sq.inch)			4052	1031.0	25.4		4050	1214	30.0	0.01
Elongation (%)	⊥	"	48.0	7.4	15.5	"	45.5	6.7	14.6	2.30*
			50.0	7.5	14.9		54.0	9.9	18.4	3.0*
Stitch tear strength (lb/inch)	∥	"	1361	235	17.3	"	1417	303.0	21.4	1.3
	⊥		1481	223	15.1		1459	262.2	18.0	0.58
Tongue tear strength (lb/inch)	∥	"	348	77.0	22.1	"	334	87.5	26.1	1.0
	⊥		355	83.2	23.4		352	81.0	23.0	0.23
Grain cracking strength (lb./sq.inch/inch)		"	10185	3526	34.6	"	10438	4304	41.2	0.42
Bursting strength (lb./sq.inch/inch)		"	14132	3546	25.1	"	14306	3567	24.9	0.31

4.2 Discussion

The leather making potentiality of market quality fallen hides collected from Northern and Southern India has been ascertained and compared with that of market quality. Slaughtered hides. It is quite apparent from the visual and histological assessment of the raw hides that fallen hides are comparable to the slaughtered hides in raw quality. The average tensile strength being roughly identical, the percent elongation appears to be slightly higher in acetone dried fallen hides. Chemical analysis of the raw hides also does not reveal any significant difference between the fallen and slaughtered hides.

Visual assessment of the finished leathers indicated that leathers produced from market quality fallen hides compare quite well with the leathers from slaughtered hides. Physical properties and chemical composition of the leathers also support this observation. The present investigation thus supports the view expressed in the previous study (3 - Ch IV) that the leather making potentiality of fallen hides depends on their raw quality i.e. if the qualities of the fallen raw hides are comparable to those of slaughtered raw hides, their leather making potentialities are also comparable and that there is no inherent difference between the two types of hides. It has already been pointed out that fallen hides are often sold in Indian market according to their quality and so very poor quality hides are not generally brought to the market and hence the better quality fallen hides are obtained from the market.

Analysis of the physical properties by statistical method reveals that the difference values are insignificant both for tensile strength and elongation of market quality slaughtered and fallen hides (Table LI). The co-efficient of variation for tensile strength is comparatively higher in slaughtered hides.

It is apparent from Table LII that finished leathers from market quality slaughtered and fallen hides have insignificant difference values for different physical properties except stitch tear strength (parallel) and elongation (parallel). The coefficient of variation in respect to different physical properties does not differ to any considerable extent.

A comparison of the data obtained from statistical analysis of the physical properties of the total number of slaughtered (84 nos.) and fallen (78 nos.) hides collected from different sources shows that (Table LIII) the difference value is significant for tensile strength (perpendicular) in favour of slaughtered hides but is insignificant for elongation.

When comparing the physical properties of the total number of leathers obtained from slaughtered and fallen hides (Table LIII) it may be seen that the different values are all insignificant on 95% level. The coefficient of variation, however, appears to be higher in leather from fallen hides for tensile strength, stitch tear strength, tongue tear strength (parallel) and grain cracking strength.

The assessment of the finished leathers produced from total numbers of slaughtered (84) and fallen (80) hides stands as follows.

	Slaughtered (%)	Fallen (%)
1st quality	14.29	21.25
2nd quality	52.38	42.50
3rd quality	27.38	15.00
Rejection	5.95	21.25

There is no difference in the area yield (% on pelt weight) of leathers from slaughtered (98.6%) and fallen (98.7%) hides.

5. Leather making potentiality of flint dried cattle hides obtained from fallen animals

5.1 Experimental procedure and results

Forty six pieces of flint dry fallen hides were collected from three of the different centres in Rajasthan State via Udaipur, Jodhpur and Jaipur. These were commercial variety of hides available in those areas produced from fallen hides.

The qualities of the commercial flint dried hides were assessed visually and are presented in Table LV.

Hides collected from Udaipur area (A) appeared to be better in primary selection than hides from other two areas and were free from flay cuts and excess flesh. But they appeared to be more contaminated on the surface with earthy matters. Hides from other two areas showed more hair slip and insect damage. All the flint dried hides were crumpled in appearance.

The flint dried hides were analysed chemically for moisture, fat and ash according to the methods reported earlier and are presented in Table LVI.

It appears from Table LVI that the moisture content of flint dried hides ranges between 14 - 21.5 percent; ash content varies from 2 to 22% and fat content varies from 1.5 - 11.5%. A higher moisture content in dried hides indicates inadequate drying. Such a high percentage of ash in flint dry hides is rather unexpected. In case of dry hides the ash content should be low but most of the hides and particularly from Udaipur area were full of earthy silicious matter and certain amount of salt. This high ash content indicates nothing but adulteration of hides just to increase the weight as the flint dried hides are sold on weight basis. The variation in fat content is also significant but such a variation may be possible depending on a number of factors like feed, breed, season and cause of death.

During processing the hides were soaked overnight in a pit containing sufficient quantity of water. Next day, soaking was continued in a fresh liquor containing 0.125% sulphuric acid, 3% common salt and 0.05% sodium trichlorophenate (all on volume of water). On the third day the hides were taken out, broken over the beam, dry drummed for 2 hr. and were put to a fresh soaking bath prepared as in the previous day. On the fourth day the hides were taken out, green fleshed and cut into sides along the line of backbone. The hides were finished into full chrome shoe upper leathers following standard procedure described in Chapter I.

TABLE LV

Visual assessment of the quality of commercial flint dried hides

Centre of collection	No. of hides	Gradation of hides			
		First	Second	Third	Rejection
A	20	-	5	10	5
B	6	-	1	5	-
C	20	-	1	12	7
Total of 3 centres	46	-	7	27	12

TABLE LVI

Chemical analysis of the flint dried hides

Centre of collection		Moisture	Ash	Fat
A	Maximum	20.0	22.0	11.5
	Minimum	14.5	4.0	1.5
	Average of 20 hides	17.0	12.7	5.3
B	Maximum	17.0	18.0	9.0
	Minimum	14.0	6.0	4.0
	Average of 6 hides	15.5	9.5	6.9
C	Maximum	21.5	18.0	11.0
	Minimum	14.0	2.0	4.0
	Average of20 hides	17.5	8.7	7.6
	Average of 46 hides	17.0	10.5	6.5

TABLE LVII

Assessment of quality and area yield of upper leathers finished from flint dried hides

Centre of collection	No. of sides	Prime	Second	Third	Printed	Rejection	Area (sq.ft) of leather per lb. of dry hide
A	40	-	12	9	11	8	1.79
B	12	-	2	5	2	3	2.37
C	40	-	2	10	13	15	2.04
Total of 3 centres	92	-	16	24	26	26	1.93

During soaking it was observed that the soaked weight of hides from Udaipur area is about 200% of that of dry weight whereas in hides from other areas it was comparatively more. After liming many of the hides demonstrated considerable putrefactive grain damage, insect damage on the grain and blister. Grain cracking was also noted in many hides along the lines the hides were folded after drying.

Finished leathers were assessed as before depending on their quality and are presented in Table LVII.

The qualities of the finished leathers produced from commercial flint dried hides appear to be rather poor. They suffer considerably due to grain damages, tick and vein marks, blisters and insect damages. Flint dry hides from Jaipur area have produced inferior types of leathers. The gradation of the leathers was found to differ slightly between the right and the left sides of the same hide. In fallen hides such a variation between two sides is quite probable. The side of the hide that remains in contact with the ground is affected more either due to mechanical damage or patchiness due to congealed blood. In the present classification certain leathers that are graded as printed leathers are rejections in the true sense but can be finished into leathers having printed grain.

Physical properties of the leathers produced from flint dried hides are tabulated in Table LVIII.

Although there appears to be considerable variation in physical properties in between the leathers, the average physical properties of the leathers are well within the normal range.

A statistical analysis of the variation in physical properties of the leathers obtained from flint dry fallen hide from that of leathers from slaughtered hides (slaughter house) is presented in Table LIX.

5.2 Discussion

Flint dried fallen hides, collected from three different areas of Rajasthan State as random samples, thus appears to be (i) stale and poor in quality with no firsts, 15.22% seconds, 58.69% thirds and the rest as

Table LVIII

Physical properties of the leathers produced from flint dried hides

Centre of Collection		Tensile strength (lb./sq.inch) ⊥	Tensile strength (lb./sq.inch) ‖	Elongation (%) ⊥	Elongation (%) ‖	Stitch tear strength (lb./inch) ⊥	Stitch tear strength (lb./inch) ‖	Tongue tear strength (lb./inch) ⊥	Tongue tear strength (lb./inch) ‖	Slit tear strength (lb./inch) ⊥	Slit tear strength (lb./inch) ‖	Grain cracking strength (lb./sq.in/in.)	Bursting strength (lb./sq.in/in.)
A	Maximum	6143	5521	56.0	56.0	1778	1943	406	557	838	1041	14136	17855
	Minimum	3018	1778	31.0	25.0	1104	870	233	233	423	411	4572	6004
	Average of 20 leathers	4057	3358	47.5	41.5	1400	1326	311	367	566	678	8991	13319
B	Maximum	5654	5418	50.0	44.0	1557	1385	328	346	677	656	20108	20108
	Minimum	2861	2199	30.0	27.5	1219	727	185	185	346	427	10372	11218
	Average of 6 leathers	4312	4003	42.0	40.0	1351	1209	261	260	530	547	15380	16756
C	Maximum	6186	6025	65.0	47.5	1693	1551	372	406	801	823	19473	20320
	Minimum	2485	1911	37.5	25.0	711	676	152	169	435	346	5443	8678
	Average of 20 leathers	4267	3584	51.5	41.0	1237	1247	263	300	471	572	10958	14095
	Average of 46 leathers	4182	3540	50.5	41.0	1322	1276	283	323	520	614	10747	13927

Table LIX

Statistical analysis of the physical properties of the leathers obtained from flint dry fallen hides and slaughtered hides collected from slaughter houses

Physical properties		Slaughtered				Fallen(flint dried)				
		No.of samples	Mean	s.d.	c.v	No.of samples	Mean	s.d.	c.v.	d-value
Tensile strength (lb/sq.inch)	∥	48	3856	950.0	19.8	46	3540	985.1	7.8	1.59
	⊥		4301	1200.0	27.9		4182	992.0	23.7	0.25
Elongation (%)	∥	"	50.0	8.4	16.0	"	41.0	6.2	15.1	7.50*
	⊥		51.0	7.5	14.7		50.5	8.0	16.1	0.30
Stitch tear strength (lb/inch)	∥	"	1410	317.0	22.5	"	1276	259.1	20.3	2.4*
	⊥		1535	243.3	15.8		1322	217.1	16.4	3.6*
Tongue tear strength (lb/inch)	∥	"	379	68.3	18.0	"	323	79.9	24.7	3.6*
	⊥		384	79.5	20.7		283	63.4	22.4	6.8*
Grain cracking strength (lb/sq.inch/inch)		"	10078	3943	39.1	"	10747	3955	36.8	0.82
Bursting strength (lb/sq.inch/inch)		"	14167	3588	24.6	"	13927	2933	21.0	0.30

rejections (ii) have a high ash content accountable only of adulterated with earthy matter resulting in poor yield. The variation of ash and fat is also large making it difficult for the tanner to give a uniform treatment and obtain uniform quality.

Classification of the finished leathers produced from flint dry hides reveals that out of 92 sides only 17.39% may be graded into seconds, 26.52% are graded into thirds and the rest are graded as rejections (including printed). The major defects that are found present in leathers from flint dry hides are putrefactive grain damage, vein and tick marks, blisters, draging marks, insect damage and grain crackiness in the folds.

In spite of the poor selection of the finished leathers the average physical properties of the leathers are well within the limit for average quality chrome upper leathers although the range of variation in different properties may be broader.

As slaughtered hides are not generally available in India in flint dry condition, data on statistical analysis of the physical properties of the leathers from flint dry hides are compared with that of the leathers from wet salted slaughtered hides (3 Ch.-IV) collected from slaughter houses (Table LIX). It may be noted that difference values are significant for elongation (parallel), stitch tear strength and tongue tear strength in favour of slaughtered hides but are insignificant for other properties.

6. Comparative study of the leather making properties of cattle hides cured in different ways

6.1 Experimental procedure and results

Slaughtered cattle hides were collected from Madras slaughter house in the afternoon. Each hide was cut into two sides and weighed. All the left sides were wet salted in the evening and considered as control sides. The right sides were cured in 3 different ways (i) flint drying, (ii) suspension drying on frame and (iii) dry salting.

Flint drying: Flint drying was done in three different ways.

(a) Six sides were taken and kept in hide cellar (10°C) in the evening. Next morning the sides were spread over the wooden platforms placed on the ground and exposed to the sun for drying. The temperature variation throughout the day ranged between 41° and 29°C. The sides were dried consequtively for the 2nd and 3rd days and stored for one month.

(b) Three sides were taken and spread over the wooden platform in the same evening. The sides were dried in the shade for three days.

(c) Three sides were taken as before and were kept in hide cellar for the night. Next morning they were green fleshed, spread over wooden lattice platform, kept in slanting positions and dried in the shade. In the evening the sides, dried incompletely, were kept in the hide cellar to prevent bacterial degradation if any. Next day the sides were dried as before in shade and kept in the hide cellar in the evening. On the third day the sides were completely dried.

Suspension drying on frame

Six sides were stored in the hide cellar in the evening Next morning the sides were framed on wooden frame by tying the edges with rope through punched holes. The sides were stretched uniformly under light tension. The frames were then placed in East West direction in slanting position under open sun at a temperature range of 41° and 29°C. The sides were dried in about two days' time.

Dry salting

Six experimental sides were salted with common salt in the usual way. After three days, the sides were nailed on wooden boards and kept in the sun at an inclination to the sun rays. The sides were dried in three days.

During processing dry and frame dry sides were left overnight in water for soaking. Next day they were re-soaked in a pit containing 0.125% sulphuric acid and 3% salt (on volume of water) and 0.05% sodium trichlorophenate. On the third day, the sides were taken out, broken over beam and put to a fresh soaking bath of the same composition. On the fourth day, they were taken out and limed in the usual way (Chapter I). The sides were finished into full chrome upper leather following the standard procedure.

Dry salted sides were put in soak water in the morning. Next day, they were broken over beam and left in a pit containing 0.05% Triton X 100 and 0.05% sodium trichlorophenate (on volume of water). Following day in the afternoon they were ready for liming.

The wet salted sides were soaked for about 4 to 5 hr. washed and limed as usual along with the experimental sides.

Observations during processing: It was found that flint dried sides took more time for soaking than the frame dried and dry salted sides. Even after 4 days' soaking, the flint dried sides had some regions which were undersoaked. It was noted after soaking and more so after liming that flint dried sides were damaged due to putrefaction in regions which remained hard after soaking and also in some other areas. In few cases the damage was severe and the sides were unsuitable for finishing.

Tannery yields of flint dried, frame dried and dry salted sides along with the corresponding wet salted sides (control) were noted during processing and are given in Table LX.

After soaking the dry sides are found to be much less soaked than the control wet salted sides (Table LXI). After liming, however, there is not much difference in pelt weight between the experimental and control sides.

Visual assessment of the leathers for quality and area yield are presented in Table LXI

An analysis of Table LXI reveals the efficiency of the different procedures for drying. Sides flint dried in hot sun (experiment a) have produced very poor quality leathers as all the sides are found to be damaged severely due to blisters and probably putrefaction. Fig.18 represents two such damaged sides after liming. Flint drying at high temperature has resulted in producing such poorly cured stock. Leathers obtained from sides that are left at room temperature (28-30°C) throughout the night and dried next day in the shade (experiment b) are

TABLE LX

Tannery yields of the sides dried in different ways
(yield calculated as % on green wt.)

EXPERIMENTAL				CONTROL		
Type of cure	Dry wt.	Soaked wt.	Pelt wt.	Wet salted wt.	Soaked wt.	Pelt wt.
Flint dry (average of 12 sides)	33.05	84.95	76.69	79.36	100.21	78.29
Frame dry (average of 6 sides)	32.65	82.14	78.06	76.00	91.00	76.50
Dry salted (average of 6 sides)	50.47	84.43	79.25	67.43	95.87	81.65

TABLE LXI

Assessment of quality and area yield of leather obtained from hides cured in different ways

Type of cure	EXPERIMENTAL					Type of cure	CONTROL				
	GRADATION				Area yield (sq.ft/lb. of green hide)		GRADATION				Area yield (sq.ft/lb of green hide)
	1st	2nd	3rd	Rej.			1st	2nd	3rd	Rej.	
Flint dry						Wet salted					
Expt. a	-	-	1	5	0.90	"	1	5	-	-	1.0
Expt. b	-	-	2	1	0.68	"	1	2	-	-	0.76
Expt. c	-	2	1	-	1.0	"	-	2	1	-	1.10
Frame dry	2	3	1	-	0.97	"	2	3	1	-	0.94
Dry salted	-	2	4	-	0.94	"	-	4	2	-	0.99

also damaged considerably. Overnight post-mortem delay and slow drying in the shade are probably responsible for bacterial degradation of the sides. Leathers produced from flint dried sides dried by the improved procedure (expt.c) are found to be rather comparable to that of control wet salted sides. Green fleshing, keeping overnight at a lower temperature (10°C) and shade drying allowing free passage of air have made this considerable improvement in the quality of the dry stock.

It is worthy to note that frame drying, even at a very high temperature (same as in expt.a) has produced well cured sides and when converted into leather they are found to be of same grade like that of control sides. Control leathers may, however, be slightly more full than experimental leathers. This very clearly shows the superiority of frame drying method over that of flint drying.

Leather produced from dry salted sides are found to be slightly inferior than control leathers. This may be due to the fact that during drying the sides are nailed on wooden boards and have no air circulation on both sides. In a later study it has been noted that dry salting in frame gives well cured hide and the leather produced from it is comparable to that of control one.

Area yield of leather (per lb. of raw hide) appears to be slightly less in case of flint dried and dry salted sides but is slightly more in frame dried sides than those of the corresponding control leathers.

Certain physical properties of the leathers obtained from experimental and control sides are given in Table LXII.

It appears that tensile strength of the leathers from flint dried sides is somewhat lower than corresponding leathers; other properties e.g., stitch tear strength, tongue tear strength, grain cracking strength and bursting strength remain practically unaffected. No significant difference in physical properties may be noted between the leathers from experimental frame dried and dry salted sides and the corresponding control leathers.

TABLE LXII

Physical properties of the leathers from hides cured in different ways

Types of cure	Tensile strength (lb/sq.inch) ⊥	Tensile strength (lb/sq.inch) =	Elongation (%) ⊥	Elongation (%) =	Stitch tear strength (lb/inch) ⊥	Stitch tear strength (lb/inch) =	Tongue tear strength (lb/inch) ⊥	Tongue tear strength (lb/inch) =	Grain cracking strength (lb/sq.inch/inch)	Bursting strength (lb/sq.inch/inch)
Flint dry (average of 12 sides)	3031	2690	47.0	43.0	1454	1294	309	306	8817	11494
Control	3376	3440	41.0	47.0	1466	1453	330	345	7571	11974
Frame dry (average of 12 sides)	4618	3731	50.0	44.0	1347	1503	290	317	10012	13700
Control	4781	3953	44.0	44.0	1322	1422	313	310	8844	12809
Dry salted (average of 6 sides)	4280	3495	51.0	45.0	1553	1455	329	302	10188	13705
Control	4057	3469	41.0	46.0	1519	1358	345	330	9827	12585

Discussion

In the present study the leather making properties of flint dried, suspension dried and dry salted sides are compared with those of corresponding wet salted sides. Although drying of hides appears to be so simple, it is really a difficult job to do in all places and in different seasons and so the success of drying method depends on environmental conditions. Experimental dry hides are stored only for a period of 1-2 months and under careful observation and thus they are kept free from any insect damage. Proper care is taken during soaking of the dry and dry salted sides.

In the course of the present investigation, it has been experienced that the following factors play significant role in proper drying of the hides.

(i) Temperature and humidity existing during drying

(ii) Post mortem period

(iii) Presence of fatty and adipose tissue layer

(iv) Free circulation of air on both sides of the hide

To produce a good dry hide proper considerations are to be given to all the above aspects, otherwise it would be a better proposition to cure the hides and particularly the fallen hides by dry salting or by wet salting. In fact, if it is not intended to store the hides for a considerably longer period, hides may better be cured by wet salting method. To produce quality dry cured stock frame drying method should be followed.

7 Summary and conclusion

1. The leather making property of hides obtained from dead animals (fallen hides) was investigated for making full chrome shoe upper leather and was compared with that of hides from slaughtered animals (slaughtered hides). Random samples of fallen hides were collected from Flaying and Carcass Utilization Centres and slaughtered hides from slaughter houses in the Eastern and Western regions of India. The quality of fallen hides appeared to be poorer than that of slaughtered hides because of factors

such as considerable delay in flaying and curing and improper handling but the selection of the finished leather compared well with that of raw selection. On the other hand, assessment of finished leathers produced from slaughtered hides was found to go down due to appreciable flaying defects and tick, pock and vein marks.

On an average, the slaughtered hides and leathers (made from slaughtered hides) possessed slightly higher tensile strength and slightly lower elongation than the fallen hides and leathers (made from fallen hides). Grain cracking strength and bursting strength of the leathers produced from fallen hides of Western region were lower in comparison to those of slaughtered hides from the same region, but it was not so in case of fallen hides of the Eastern region. Chemical analysis of raw hides and finished leathers did not show marked difference between the slaughtered and fallen hides.

2. Market quality fallen and slaughtered hides were collected from different centres in Northern and Southern regions of India and were converted into full chrome shoe upper leather; the leather making potentiality of fallen hides was compared with that of slaughtered hides. Market quality fallen hides were found to be roughly of the same quality as the slaughtered hides. The qualities of finished leathers produced from fallen and slaughtered hides were also comparable. It is thus apparent from the above investigations that the leather making property of fallen hides is dependent on their quality in the raw state and that there is no inherent difference between fallen and slaughtered hides arising simply out of the fact that the animal is fallen or slaughtered.

Physical properties of the slaughtered and fallen hides and of the leathers produced from them were analysed statistically and the difference values between slaughtered and fallen hides were determined.

3. Leather making potentiality of the market quality flint dried cattle hides prepared from fallen hides by conventional method was investigated. It was observed

that such flint dried hides were mostly poor in quality and about 80 percent of them were found unsuitable for full chrome shoe upper leather. Some of the hides could better be finished into corrected grain or printed leathers. Many of the hides suffered from the defects those were common to the fallen hides and to flint dried hides. Soaking back of the flint dried hides was also rather difficult. Average physical properties of the leathers from flint dried hides were found to be comparable to that of average physical properties of leathers produced from slaughtered hides.

Statistical analysis of the physical properties of the leathers obtained from flint dried hides was compared with the statistical data obtained from slaughtered hides.

4. The qualities of chrome upper leathers produced from flint dried, frame dried and dry salted sides of cattle hides were compared with the corresponding leathers from paired wet salted sides. Of the different methods of drying, suspension drying on frame produced the best quality raw stock and the upper leathers produced from such sides were comparable to the leathers from wet salted sides. Flint dried sides produced by conventional method were severely damaged during processing. The quality of dry hides could be improved by frame drying and taking specific measures during drying. Tensile strength of the leathers was slightly affected by flint drying, the other physical properties remaining practically unaffected by different methods of drying.

CHAPTER V

1. Sole leather making potentiality of fallen and slaughtered buffalo hides and proper utilisation of buffalo hide offals

2. Methods

2.1 Visual assessment of raw hides

The hides were shaken off the excess salt and visually examined taking into account various factors like (i) general appearance (ii) flay cuts e.g. holes, deep and light cuts (iii) grain damage due to sores, abrasion, scratches and putrefaction, (iv) curing defects e.g. hair-slip, red-heat, etc. and (v) substance.

2.2 Rapid tanning of sole leather

Vegetable tanned sole leathers were generally manufactured following conventional time consuming processes. For sometime past, tanners were more concerned about the cost of labour, space in the tannery and quick turn over and so the recent trend in sole leather manufacture is to shorten the tanning period. Different rapid tanning techniques had been suggested from time to time but very few of them are commercially followed as sole leather manufacture varies from country to country and from tannery to tannery depending on a number of variable factors e.g. type of tanning material available, quality and weight range of raw materials, temperature of tanning, quality of the leathers required and so on.

It has generally been emphasised that unless the grain is conditioned by some pretanning treatment rapid tanning may result in pebbling of grain. Condition of the pelt i.e. plumpness has been the point of consideration by some investigators[92,93,94]. Shuttleworth[95] recommended pickling of pelt with sulphuric acid and salt to achieve quick tannage. Different pretannages were also advocated to produce rapid tanned sole leather. To adopt a standard rapid tanning method to be followed in the present investigation, the performances of some of the old and new processes were examined and the convenient one was accepted.

Besides pit tanning process, bag tanning process is also followed in India by the small and village tanners.

The commercial bag tanned leathers are not properly tanned so as to give the chemical and physical properties of good sole leather though this method of tanning is quite rapid. So bag tanning technique was also used in modified form to produce rapid tanned sole leather.

Based on the above information a rapid tanning process was worked out and followed in subsequent studies.

2.3 Visual assessment of leather quality

The quality of the sole leathers were assessed visually on the basis of the following:

(i) general appearance (ii) colour (iii) uniformity (iv) flexibility (v) pipeyness (vi) crackiness and (vii) gloss.

2.4 Physical properties

Samples were taken from sampling positions of the sole leathers and were examined for certain physical properties (i) abrasion (ii) water absorption and (iii) apparent density.

2.5 Value index for leather

The value index for the different types of leathers made from buffalo hide offals was calculated from the equation

$$\frac{V1 \times Y}{Vr}$$

Where V1 is the market value of the leather per Kg. or per sq.ft. of leather, Y is the yield of leather per kg. of raw hide and Vr is the price of raw hide per Kg.

3. Standardization of a rapid tanning method for sole leather manufacture

3.1. Experimental procedure and results

Wet salted buffalo hides, weighing about 40 - 50 lbs. were taken for sole leather tannage.

3.1.1 Process 1

Wet salted buffalo hides were cut into sides, washed and soaked overnight in a pit and then limed for 3 days.

in a liquor containing slaked lime - 15%, sodium sulphide - 0.5%, once used lime liquor 50% and water 250% (all on soaked weight). On the 4th day the sides were unhaired and relimed with slaked lime - 15%, sodium hydroxide - 0.5% and water 500% for 3 more days and then fleshed, weighed and left overnight in plain water. Next day they were delimed partially with 0.5% ammonium sulphate and then treated with 0.5% naphthalene sulphonic acid for about 1½ hr. The sides were then put into the tan liquor at 8°Bk and handled properly. The liquor was made up of 3 parts wattle extract and 1 part myrobalan extract. The sides were daily transferred to pits containing liquor of higher Bk strength as given below:

8° - 10° - 12° - 15° - 20° - 25° - 35° - 45° - 55° - 65° - 70° Bk.

In case of heavy hides, further tanning could be done in drum by drumming for 2 hr. at 75°Bk, the next 2 hr. at 85°Bk and the last 2 hr. at 100°Bk. Tanning started at pH 4.5 and was over at 3.7 - 3.8. After the completion of tanning the leathers were piled for two days. Leathers were then washed well, bleached and then treated in a myrobalan liquor (30°Bk) for a day or two, washed and loaded. The leathers were then oiled in a drum, set out and dried. Finally the leathers were seasoned and rolled.

3.1.2 <u>Process II</u>

In this process a sodium acetate pretreatment was given before tanning. Wet salted buffalo hides were taken, soaked and limed as in process I and were delimed completely with ammonium sulphate. Delimed pelts were treated in a drum with sodium acetate - 4%, sulphuric acid - 1.5%, salt - 8% and water 300% and left overnight in the bath. The pelts were then washed thoroughly, put to a liquor of 12° Bk and transferred daily to a liquor of increasing strength upto 50°Bk (12° - 20° - 30° - 40° - 50° Bk). The strength of the liquor was then increased by 10°Bk in every alternate days. Tanning was completed in 70°Bk liquor and the tanned pelts were kept in pile for 2 days. After piling the leathers were finished as in process I.

3.1.3. Process III

In this process completely delimed pelts were treated with formaldehyde before they were put to the tan liquor. After normal soaking the buffalo sides were limed[96] in a pit containing sodium sulphide - 3.5%, caustic soda - 2% and water 300%. No lime was added. The sides were handled properly and left overnight in the liquor. Next day they were unhaired, scudded fleshed and weighed. They were washed and delimed completely with 1% ammonium sulphate and 0.5% sulphuric acid and 250-300% water. Next day the delimed pelts were scudded again and then treated overnight with 1% formaldehyde and 300% water. On the following day they were rinsed in water and tanning started at 12°Bk liquor. The sides were transferred daily as in process II upto 50°Bk liquor. They were then taken in a drum, containing 70°Bk liquor and drummed intermittently for the day. In the evening they were taken out and put in a pit containing 70°Bk liquor. After tanning, leathers were piled outside for 2 days. The following procedures to finish the leathers were the same as in process I.

3.1.4 Process IV

In this process the delimed pelts were treated with a buff r salt mixture[97] before tanning. Soaking and liming were followed as in process III. The pelts were then delimed completely with ammonium sulphate - 1%, sodium bisulphite - 1%, boric acid - 1% and water - 300% by leaving the pelts overnight in the pit. The pelts were then treated with the following buffer salts (16.5% on pelt wt.) taken in a drum containing 100% float. The composition of the salt mixture was as follows:

Sodium sulphite	-	38.6 parts
Sodium thiosulphate	.	8.0 parts
Disodium phosphate	-	16.6 "
Sodium formate	-	12.0 "
Boric acid	-	3.9 "
Borax	-	15.9 "
Phthalic anhydride	-	3.1 "
Oxalic acid	-	1.9 "

The drum was run for 4 hr. and left overnight in the bath. Next day the drum was run again for 1 hr. pH was checked to be about 7-8. Tanning was then started in the drum. A total of 32% tannin extract (wattle extract - Kenmosa brand) was used for tanning.

3% extract was fed into the drum along with the pelt and the buffer salt solution and drummed for 3 hr. . In the second and third instalments 4% and 5% extracts were added and drummed for 3 hr. in each case and then left overnight in the liquor. Next day 6%, 7% and 7% of the extracts were fed into the drum by three instalments and drummed for 3 hr. in each case. It was expected that penetration will be over but a thin streak was left in the central layer of the sides. Additional 2 days were required for complete penetration. The sides were washed free from buffer salt and run in formic acid for 30 mt. and then retanned with 115°Bk liquor of the same extract. The drum was run intermittently for 2 days. The leathers were then kept piled for 2 days. Bleaching and finishing were done as usual.

3.1.5 <u>Process V</u>

In this process tanning was done by a modified bag tanning method a typical process followed in India. Soaking and liming of buffalo sides were done as in process III. The sides were scudded and delimed completely by treating overnight in a pit with 1% ammonium sulphate and 0.5% sulphuric acid. Next day they were washed well with water and put to the 'malni' liquor which was constituted of a used 10°Bk liquor. The delimed pelts were handled properly in the 'malni' liquor for two days whereby the grains of the pelts were conditioned and became suitable for stitching into bags. Each bag was then filled up with 25°Bk liquor made up of spray dried wattle extract. The bag was kept filled with the liquor throughout the day and kept in the liquor overnight in the pit. Next day, the bags were hung up again and filled with the liquor as before. On the third day the bags were reversed and tanning continued in the same way for one day more. Next day the bags were cut out, trimmed and left in the liquor overnight. It may be pointed out that complete penetration may be possible within three days in thinner sides but may take 2 days more for comparatively thicker hides.

Next day the sides were drum tanned with 15% spray dried wattle extract. The extract was fed into the drum in dry form by three instalments and the drum was run for 5 hours. Next day another 15% extract was fed in and drummed. The tanned pelts were taken out and piled overnight. Next day the leathers were drummed with 1% formic acid; and then processed and finished as before.

3.1.6. Process VI.

In this process tanning was done at a lower pH adjusted with sodium hydrosulphite and formic acid. Buffalo sides were soaked and limed as in process III. Pelts were then washed in a paddle for one hour and scudded and left overnight in a pit containing plain water. They were scudded once again and transferred to a pit containing 10° Bk liquor made by dissolving wattle extract. 2% sodium hydrosulphite and 1% formic acid were added to the liquor. The pH of the bath was adjusted to 3.5. The sides were handled in this pit twice, once in the morning and once in the evening. On the second day pH was adjusted to 3.5 with 0.125% formic acid and the sides were handled as before. In the third day the sides were transferred to a pit containing 50° Bk liquor of wattle extract. The pH of the liquor was adjusted to 3.5 with 0.5% formic acid and 1% sodium hydrosulphite. The sides were handled in this pit for 2 days. On the fifth day the sides were transferred to a pit containing 75° Bk liquor of wattle extract. pH was adjusted to 3.6 - 3.7 with 0.5% formic acid and 1% sodium hydrosulphite. Next day the sides were handled in the same liquor.

On the 7th day sides were drummed in a liquor of 120° Bk (100% float), pH being adjusted with 0.25% formic acid to 3.6 - 3.7. The sides were drummed intermittently for the whole day and piled on for one day. The sides were then washed and then bleached, and oiled in a drum. Next day they were well set and then dried. After drying the leathers were seasoned and rolled.

Chemical and physical properties of the leathers are presented in Tables LXIII and LXIV.

3.2. Discussion.

It may be noted ~~from Table~~ that chemical composition of the leathers are quite comparable to each other and are in conformity with the chemical properties of the Indian sole leathers reported earlier(98) except the water solubles which are comparatively higher in these leathers. But recently reported(94) (99) values for water solubles of rapid tanned sole leathers are indentical with the present values.

The physical properties of the leathers produced by different methods also do not vary to a great extent. It is apparent that first two processes are rather lengthy. Processes III and IV are moderately rapid and produce good leathers but process IV requires more careful observation and involves more cost. Process V although rapid gives less yield (due to trimming) and is somewhat complicated. Retanning of bag tanning leather may, however conveniently be followed by Indian tanners who follow bag tanning process. Judging from tanners point of view (e.g. colours, flexibility, etc.) leathers produced by process VI were considered best of the different lots and this process is a fairly rapid one producing quality sole leathers within 13-14 days' time.

Process VI was, therefore, accepted as the standard process for making sole leather and was followed in the present investigation.

4. Comparative study on the quality of sole leathers from fallen buffalo hides collected from Flaying and Carcass Utilization Centre and slaughtered buffalo hides collected from slaughter house.

4.1. Experimental procedure and results.

25 slaughtered buffalo hides (average wt. range 59.5 lbs.) from Bombay slaughter house and 25 fallen hides (average wt. range 61 lbs.) were collected from the Flaying and Carcass Utilisation Centre, Bombay.

The hides, received in wet salted condition,

TABLL LXIII

Chemical analysis of sole leathers made by different methods

Chemical analysis (as received)	Process Nos. 1	2	3	4	5	6
Moisture (%)	11.5	12.6	10.7	12.7	11.9	13.4
Fat (%)	3.16	3.03	2.5	1.4	2.9	2.7
Water solution (%)	15.4	14.0	13.6	13.2	13.61	14.8
Insoluble ash (%)	0.1	Negligible	0.3	Negligible	Negligible	Negligible
Hide substance (%)	40.74	41.86	40.0	41.58	41.16	40.2
Fixed tan (%)	28.65	28.51	32.7	31.12	30.43	30.9
Degree of tannage (%)	70.32	68.10	81.75	74.84	73.93	76.87
PH of water solubles	3.3	3.6	3.3	3.7	3.4	3.5

General characteristics and physical properties of sole leathers made by different methods

Physical properties	Process Nos. 1	2	3	4	5	6
Colour	Light biscuit	Golden	Biscuit	Pink with tendency to become reddish on ageing	Light pink	Light biscuit
Flexibility	Fairly flexible	Less flexible	Fairly flexible	Quite flexible	Flexible	Flexible
Tensile st. (lb/sq.inch)	I 5765 II 6474	6125 5674	5126 4669	4420 5363	4519 4194	6935 5958
Leather yield (% on pelt wt.)	55-60	55-60	55-60	55-60	53-58	55-60
Abrasion (inch/500 R)	0.062	0.065	0.060	0.055	0.06	0.07
Apparent density	0.91	0.99	0.93	0.88	0.92	0.95
Water absorption (%)	½h. 34.9	44.5	38.2	36.2	30.8	32.0
	2h. 38.6	47.2	41.2	39.0	35.4	37.0
	24h. 39.1	47.7	41.9	39.7	37.2	39.0
Tanning period (from raw to finish)	28-30 days	26-28 days	17-19 days	17-19 days	14-16 days	13-14 days

were examined for their qualities. The hides were shaken off the excess salt and assessed for their quality by visual inspection. Observations are recorded in Table LXV.

It may be noted from Table LXV that of the 25 slaughtered hides, 9 hides are graded as **first**, 10 as second and 6 as third quality. On the other hand, 3 fallen hides are graded as **first** quality, 8 are seconds, 13 are thirds and one of them is of rejection quality.

Vegetable tanned sole leathers were produced according to thestandard process. During liming operation it was noticed that most of the fallen hides had either blood patches or a net-work of blood marks due to the presence of congealed blood along the network of veins. Figs. 19 and 20 represent such network of veins and different patches due to blood and possibly other pigmented materials that could not be removed during normal pretanning processes. It was observed that such blood patches or blood stains were more prominent on one half of the hide than the other. This is probably due to the fact that dead animals are left lying down on the ground on one side for a considerable length of time before they are taken for disposal. Fig. 21 clearly shows the contrast between two sides of the same hide after liming. The network of blood marks is apparent on the left hand side. These blood marks and other pigmented scud marks could not be removed even after tanning though they become less prominent. This may be seen in Fig. 22 which depicts an unfinished leather i.e., after pit tanning and before drum tannage. Such patches and marks, if present, do appreciably devalute the leather quality although other properties of the leathers remain unaffected. Such patch marks were found absent in the slaughtered hides.

Table LXVI represents the sole leather yield of the slaughtered and fallen hides.

On an average, slaughtered hides give about 60% yield on pelt weight and the fallen hides yield about 59%. It is of interest to note that leather yield when calculated on raw weight is about 79% in case of slaugh-

TABLE LXV

Visual assessment of the quality of raw buffalo hides.

Grades	Slaughtered		Fallen	
	Sample Nos.	No. of hides	Sample Nos.	No. of hides
First	6, 8, 9, 11, 15, 17, 18, 19 & 21	9	14, 23 & 25	3
Second	2, 3, 4, 10, 13, 14, 20, 22, 23 & 24	10	5, 6, 8, 10, 12, 16, 19 & 22	8
Third	1, 5, 7, 12, 16 & 25	6	1, 2, 3, 4, 7, 9, 11, 15, 17, 18, 20, 21 & 24	13
Rejection	--	Nil	13	1
General obervations	The slaughtered hides were properly cured, well fleshed and free from putrefaction and grain damage. But many of these hides were damaged due to flay cuts which lowered their qualities.		The fallen hides were free from flay cuts but retained a good amount of adhering flesh. One hide is found to be degraded to rejection quality due to putrefactive grain damages.	

tered hide and about 6% less in the case of fallen hides.

Leathers produced from slaughtered hides are graded as follows: 7 firsts, 11 seconds, 5 thirds and 2 rejections. 2 pieces of leathers are graded as rejections because of deep flay cuts and incidence of grain crackiness in one side. In the case of leathers from fallen hides 2 are graded as firsts, 6 as seconds, 10 as thirds and 7 as rejections.

Data presented in Table LXVII show that, physical properties e.g., abrasion, water absorption and apparent density of the leathers produced from slaughter and fallen hides do not differ to any great degree. On an average abrasion and apparent density appears to be slightly more and water absorption is slightly less in case of leathers from fallen hides.

4.2. Discussion.

It appears from the visual assessment of the raw hides that slaughtered buffalo hides from slaughter house are comparatively better in quality than the fallen buffalo hides collected from Flaying and Carcass Utilization Centre. After liming fallen hides demonstrate blood mark and coloured patches on the grain side which are found to be persistent even after tanning to a lesser degree. But slaughtered hides are practically free from such stains and patches.

Leather yield when calculated on pelt weight seems to be lower in case of fallen hides by about 1% than slaughtered hides which may be considered insignificant. But the difference is quite significant when calculated on raw weight and is probably due to the excess adherent flesh being present in fallen hides.

Assessment of leather quality shows that leathers from slaughtered buffalo hides stand a better selection with 28% first quality, 44% second quality, 20% third quality and 8% rejections. Where as leathers from fallen buffalo hides are graded as follows: 8% first quality, 24% second quality, 40% third quality and 28% rejections. Both in case of slaughtered and fallen

TABLE LXVI

Tannery weights (lb.) and yields (%) during sole leather processing of slaughtered and fallen buffalo hides.

Tannery weights	Slaughtered				Fallen			
	Raw wt.	Soaked wt.	Pelt wt.	Leather wt.	Raw wt.	Soaked wt.	Pelt wt.	Leather wt.
Maximum	70	83	92	58	74	87	96	58
Minimum	42	53	60	28	42	46	57	30
Average of 25 hides	59.5	69.3	78.8	47.3	61.2	66.6	75.7	44.7
Total wt.	1488	1733	1971	1182	1530	1666	1893	1117
Tannery yields (average) on								
Raw wt.	-	116.47	132.46	79.44	-	108.89	123.73	73.01
Pelt wt.	-	-	-	59.97	-	-	-	59.01

TABLE LXVII

Physical properties of sole leathers from slaughtered and fallen hides.

Type of raw hides	Abrasion (inch/400R)	Apparent density	Thickness mm.	Water absorption (%)		
				½ hr.	2 hr.	24 hr.
Slaughtered:						
Maximum	0.125	1.030	7.5	34.0	40.0	43.5
Minimum	0.081	0.866	4.4	26.0	31.5	35.0
Average of 25 leathers	0.098	0.976	6.0	30.0	35.0	39.0
Fallen:						
Maximum	0.132	1.150	7.8	32.5	39.0	44.0
Minimum	0.089	0.952	5.5	20.0	29.5	30.0
Average of 25 leathers	0.102	1.020	6.3	28.0	33.0	37.0

hides the selection of finished leathers is rather lowered as related to the raw selection. Deep flay cuts in case of slaughtered hides and blood and other patches in fallen hides are mainly responsible for such devaluation of the leathers.

Sole leathers made from slaughtered and fallen hides do not differ to any considerable extent in respect to their physical properties (i.e. abrasion, apparent density and water absorption)

5. Comparative study on the quality of sole leathers made from market quality slaughtered and fallen hides.

5.1. Experimental procedure and results.

25 slaughtered buffalo hides and 25 fallen buffalo hides were collected from Calcutta hide market in wet salted condition. The hides were trimmed in croupons, shoulders and bellies and the croupons were used for the manufacture of sole leather according to the standard process.

Buffalo hides were examined for their quality by visual inspection as before. After trimming the croupons were graded once again for quality in order to find out whether trimming had any influence on gradation in terms of hide quality. Gradation of raw hide quality is presented in Table LXVIII.

It is apparent ~~xxxxxxxxxxxx~~ that market quality slaughtered buffalo hides are much better in quality than the market quality fallen hides. No slaughter buffalo hide is found to be of rejection quality. On the other hand, 40% of the fallen hides, are of rejection quality. After trimming the croupons from the slaughtered hides are found to be considerably upgraded and the croupons of the fallen hides are upgraded to some extent. This significant improvement in the quality of slaughtered hide croupons is mainly due to the reduction in flaying defects that are confined usually to the belly areas.

It was pointed out in the earlier work (4-Ch-V) that the network like marks due to presence of congealed blood and other coloured patches were present in leathers

TABLE LXVIII

Assessment of market quality slaughtered and fallen buffalo hides before and after trimming.

Grades	Slaughtered: Assessment before trimming — Sample Nos.	No. of hides	Fallen: Assessment before trimming — Sample Nos.	No. of hides
First	1, 6 & 11	3	5, 12 & 20	3
Second	2, 3, 4, 5, 7, 8, 10, 12, 13, 16, 17, 18, 19, 20, 23 & 25	16	1, 6 & 19	3
Third	9, 14, 15, 21, 22 & 24	6	2, 4, 10, 11, 14, 17, 22, 23 & 24	9
Rejection		Nil	3, 7, 8, 9, 13, 15, 16, 18, 21 & 25	10
	Assessment after trimming		**Assessment after trimming**	
First	1, 4, 5, 6, 7, 9, 10, 11, 13, 14, 15, 16, 18, 19, 20, 21 & 25	17	5, 12, 19 & 20	4
Second	2, 3, 8, 12, 17, 22, 23 & 24	8	1, 4, 6, 22, 23 & 24	6
Third	-	Nil	2, 3, 10, 11, 14, 15, 16, 17, 21 & 25	10
Rejection	-	Nil	7, 8, 9, 13 & 18	5

from fallen hides and the general appearance of the leathers were appreciably affected due to these marks and patches. Certain modifications in the pretanning operations were therefore made in the present study with a view to overcome this defect.

(a) Normal soaking and short liming.

Salted croupons were soaked overnight in plain water and were limed with 3.5% sodium sulphide, 2% caustic soda and 300% water.

(b) Normal soaking and long liming.

Salted croupons were soaked as in previous occasion and were then limed in a pit containing 150% old lime liquor, ½% sodium sulphide, 7% slaked lime and 150% water. The sides were unhaired on the 4th day and were relimed for 3 days in the pit containing 10% lime. On the 7th day the sides were fleshed, scudded and left overnight in plain water.

(c) Acid soak and short liming.

The croupons were soaked overnight in a pit containing 0.125% sulphuric acid, 3% salt (both on volume of soak liquor) and 300% water. The pH of the bath was adjusted to 4.5. Next day the sides were limed according to the short liming process as in (a).

(d) Acid soak and long liming.

The croupons were soaked overnight in acid soak liquor as in (c) and limed for 7 days following the long liming process as in (b).

It has been observed that as in the case of the previous studies, maximum incidence of patches is found in pelts which are given a normal soak and short liming (standard process). Certain improvements are noticed when the croupons are processed by normal soak and long liming as well as by acid soak and short liming; but a considerable improvement is noted when the sides are treated with acid soak and long liming.

Tannery yields during processing the croupons from slaughtered and fallen hides are given in Table LXIX.

TABLE LXIX

Tannery weights (lb.) and yields (%) during sole leather processing of market quality slaughtered and fallen buffalo hides.

Type of raw hides	Slaughtered				Fallen			
	Raw wt.	Soaked wt.	Pelt wt.	Leather wt.	Raw wt.	Soaked wt.	Pelt wt.	Leather wt.
Maximum	25	-	-	21	38	-	-	28.5
Minimum	15	-	-	10.25	15	-	-	8.0
Average of 25 hides	22.0	24.8	26.9	16.3	27.2	27.2	29.6	18.14
Total wt.	551	619	673	407.3	679	681	741	453.5
Tannery yields (average) on								
Raw wt.	-	112.34	122.14	73.91	-	100.29	109.13	66.79
Pelt wt.	-	-	-	60.51	-	-	-	61.20

It appears from Table LXIX that sole leather yield when calculated on pelt weight is roughly the same for both the slaughtered and fallen croupons. It may further be noted that tannery yield, calculated on raw weight, is about 7% higher in the case of slaughtered croupons.

Changes in area of the croupons during sole leather tannage was recorded in case of 12 slaughtered and 12 fallen hides. The area of the croupon seems to go down (Table LXX) considerably after liming and further reduction in area takes place after vegetable tanning. After rolling, however, area of the leather increases again to the extent of about 94% of the original value in the salted condition. In respect of changes in area during processing there appears to be no difference between the slaughtered and fallen hides.

Sole leather quality was assessed visually by a commercial tanner according to the trade practice followed in his tannery. Leathers were graded into firsts, seconds and rejections. Assessment of the quality of finished leathers (Table LXXI) shows that in a general way sole leathers from slaughtered hides grade better than leathers from fallen hides. It may, however, be noted that slaughtered hides are degraded in quality to some extent in comparison to raw selection. Fallen hides, on the other hand, appear to be upgraded.

Some physical properties like abrasion, water absorption and apparent density that characterise the quality of sole leather were determined and are tabulated in Table LXXII.

Physical properties of the leathers (average values) do not vary to an appreciable extent between the leathers from slaughtered and fallen variety. Water absorption of the leathers appears to be slightly higher in slaughtered hides.

5.2. Discussion.

In the present investigation market quality slaughtered and fallen buffalo hides are compared in respect to their suitability for making vegetable tanned sole leathers. As in the previous study (44-Ch-V)) slaughtered

TABLE LXX

Variation in area yield during processing of market quality buffalo hides.

Type of raw hides	Area (sq. ft.)			
	Salted hide	Pelt	Leather (before rolling)	Leather (after rolling)
Slaughtered hides.				
Maximum	19.75	16.50	16.25	18.0
Minimum	15.0	13.0	11.50	13.25
Average of 12 hides	17.39	14.96	14.35	16.17
Total area	207.5	179.5	172.25	194.0
Average area yield (%) on				
Raw area		86.51	83.01	93.49
Pelt area		-	95.96	108.07
Fallen hides.				
Maximum	23.00	20.50	18.0	21.0
Minimum	14.50	12.00	13.25	14.0
Average of 12 hides	19.21	16.73	15.67	17.98
Total area	230.50	200.75	188.00	215.75
Average area yield (%) on				
Raw area	-	87.09	81.56	93.60
Pelt area	-	-	93.65	107.50

TABLE LXXI

Assessment of the quality of finished sole leathers made from market quality slaughtered and fallen buffalo hides.

Grades	Slaughtered		Fallen	
	No. of left sides	No. of right sides	No. of left sides	No. of right sides
First	10	11	6	7
Second	13	12	14	11
Rejection	2	2	5	7

TABLE LXXII

Physical properties of sole leathers made from market quality slaughtered and fallen buffalo hides.

Types of hides	Abrasion (inch/400R)	Apparent density	Thickness (mm)	Water absorption (%) ½ hr.	2 hr.	24 hr.
Slaughtered hides.						
Maximum	0.163	1.00	6.6	48.0	53.0	59.0
Minimum	0.083	0.85	4.4	33.0	37.0	40.5
Average of 25 leathers	0.100	0.90	5.8	37.9	42.5	47.1
Fallen hides.						
Maximum	0.110	1.04	6.6	38.5	42.0	46.0
Minimum	0.069	0.81	3.7	24.5	32.5	36.0
Average of 25 leathers	0.094	0.94	5.1	33.1	37.1	40.7

buffalo hides are comparatively better in quality than the fallen hides. The qualities of the market quality slaughtered hides are found to be upgraded by trimming off the belly areas as these regions are found to be damaged more due to flay cuts

Blood and other coloured patches that are predominently present in fallen buffalo hide and appreciably affect the general appearance of the finished sole leathers can be considerably removed by following acid soak and long liming. Hence in processing fallen hides the beamhouse operations should be modified accordingly. Probably brine curing of the fallen buffalo hides may also be advantageous in this respect.

The present investigation shows that leather yield (on pelt wt.) is roughly the same in cases of both slaughtered and fallen hides. This also supports the previous finding (4-Ch-V) that fallen hides retain more adhering flesh, etc. and so give less leather yield on raw weight basis. Area yield of leather do not vary to any considerable extent between the slaughtered and fallen hides.

As in the previous study (xxxxxxxxx leathers from slaughtered buffalo hides stand better selection than those of leathers from fallen hides. Physical properties of the leathers do not vary much between the leathers from slaughtered and fallen ones. Water absorption may be slightly less and apparent density slightly more in fallen hides.

6. Better utilisation of buffalo hide offals.

The present work was undertaken to exploit the various possibilities of utilising the buffalo hide offals and find out the type of leather or leathers that may be conveniently made out of the offals and marketed profitably.

6.1. Experimental procedure and results.

Slaughtered and fallen buffalo hides (average weight 54 lb.) that were collected from Calcutta hide market were trimmed into croupons, shoulders and belly pieces. The shoulder and belly pieces averaged 20.8 and 33.7

per cent respectively of the total weight of the hides. Butts were used in making vegetable tanned sole leather and the shoulder and belly pieces were taken for processing and the following different types of leathers were made.

6.1.1. Chrome lace leather (for woven upper)

Only the belly pieces were taken for the production of chrome lace leathers. Salted pieces were soaked overnight and then limed in a pit containing 1% sodium sulphide, 7% lime, 150% old lime liquor and 150% water. After liming for 3 days the pieces were unhaired and put into a fresh lime liquor containing 7% lime and 300% water. Next day they were fleshed, scudded, washed and delimed. The pelts were then pickled and chrome tanned in the usual way. The leathers were then shaved to an uniform thickness. After neutralisation they were dyed, mordanted with 3½% cutch extract, fatliquored with 3% anionic fatliquor and dried. After staking and buffing they were finished using conventional protein based compositions and glazed.

6.1.2. Hydraulic leather.

Shoulder pieces were taken and processed upto pickling in the same way as for lace leather. The pickled pelts were then chrome tanned with 6% chrome extract (1.5% Cr_2O_3). The leathers were sammed, levelled, neutralised uniformly to a pH of about 4.5 and fatliquored with 3% anionic fat liquor. They were then vegetable tanned with 30% extract (on shaved weight) comprising 22.5% sulphited quebracho and 7.5.% wattle extracts. After tanning they were further fatliquored with 4% anionic fat liquor and topped with about 1% cationic fat liquor. They were then set out and dried. The leathers were then finished after buffing and snuffing.

6.1.3. Upper leather.

Both belly and shoulder pieces were taken for the manufacture of upper leather. The pieces were soaked overnight and limed for 1 day using 3.5% sodium sulphide, 2% caustic soda and a float of 300%. After unhairing and fleshing the pelts were delimed partially and then pickled and chrome tanned according to the standard process. Tanned leathers were then split and shaved. They were next neutralised, fatliquored with 4% anionic fatliquor, retanned with 3% syntan (Basynton F.C., BASF) and 7% wattle extract and re-fatliquored with 2% anionic fatliquor. They were then set out, dried, staked, buffed and snuffed. The leathers were then resin finished.

6.1.4. Shrunken grain leather.

Shoulder and belly pieces were soaked overnight and limed in a similar way as for lace leather except in that thesecond liming was extended by two more days. The hides were then split, delimed completely and bated. The bated pelts were sammed and pretanned in a drum with crushed myrobalan nuts and peltophorum ferrugineum leaves followed by myrobalan extract powder. Finally the pH of the bath was lowered using formic acid. A period of about 5 hours was needed to complete the pre-tanning operation. They were then retanned with chrome extract (8%). They were then shaved, neutralised, fat-liquored with 3% anionic fatliquor and oiled. The pieces were then dried and dry-drummed. The dry-drummed leathers were boarded by hand to render the grain more prominent and then finished using acrylic binders.

6.1.5. Bunwar and kattai leathers.

Shoulder pieces were used in making bunwar leathers. The shoulder and belly pieces were soaked overnight, limed in the same way as for shrunken grain leather and delimed completely. They were vegetable-tanned using a blend of wattle and myrab extracts. Offals were put to a liquor of 10° Bk. After handling for 2 days the strength of the liquor was increased to 15° Bk. Every alternate day the strength of the liquor was increased by 5° Bk upto a concentration of 25° Bk and then by 10° Bk till it reached 45° Bk. The strength of the liquor was then increased to 60° Bk and tanning was finished in the same liquor. The leathers were lightly shaved to uniform thickness, bleached and fatliquored with 4% anionic fatliquor. They were then well set, and dubbined on the flesh side with a .1% of a mixture of tallow and fish oil. Bunwar leathers were not dubbined. Both the types of leathers were dried, buffed, snuffed and finished with protein based composition and glazed.

6.1.6. <u>Sole leather</u>.

Only the belly pieces were taken for sole leather tannage. After an overnight soaking they were limed as for lace leather except in that the second liming was extended by one day more. Pelts were delimed partially and tanned in the same way as kattai leather . The tanned leathers were bleached, loaded with 1% loading materials, fatliquored, oiled lightly, well set and dried. They were seasoned and rolled lightly.

Leather yield and the value index for the different types of leathers are presented in Table LXXIII.

6.2. <u>Discussion</u>.

In the present study the shoulders and the belly pieces of the buffalo hides are processed into different types of leathers. Assessment of each individual piece of shoulder or belly is not attempted either in the raw or finished condition. The leathers are assessed by a visual inspection and are found to be of average quality. After finishing them into various types of leathers their present market value in India are ascertained and compared.

The different types of leathers made from shoulder and belly pieces may be arranged in the following order of decreasing value index

Shoulder: Bunwar > hydraulic > upper > shrunken grain.

Belly: Kattai > Sole > upper > chrome lace > shrunken grain.

It is apparent from Table X that bunwar leathers made from shoulder pieces and kattai leathers made from belly pieces have the maximum market values and there is also a good demand for these types of leathers in India. These leathers are generally used in making chappal straps, insole for chappals, camera and transistor cases and so on.

TABLE LXXIII

Value index of different types of leathers produced from buffalo hide offals.

Type of leather produced	Type of tannage	Offals taken	Weight of salted offals taken (Kg.)	Leather yield	Total leather output (calculated on total raw wt. of belly or shoulder pieces)	Approximate market value for the total quantity of leather		Value hides VL x Y / Vr.
1. Lace leather	Chrome	Bellies	154.5	155 Sq. ft.	413 sq. ft.	@ Re.1.00	Rs. 43.00	1.23
2. Hydraulic leather	Chrome retan	Shoulders	91.0	27 Kg.	76.2 Kg.	@ Rs.9.00	Rs. 685.00	3.3
3. Upper leather	Chrome retan	Shoulders & bellies	143.0	Sh.-77 sq.ft. Bel.- 78 sq.ft. Sp.-74 sq.ft.	Sh.-360 sq.ft Bel.-365 sq.ft Sp.-345 sq.ft.	@ Rs.1.35 @ Rs.1.35 @ Re.0.50	Rs. 486.00 Rs. 493.00 Rs. 172.00 Rs.1151.00	1.82
4. Shrunken grain leather	Semi-chrome	Shoulders & bellies	136.0	Sh.-50 sq.ft. Bel.-65 sq.ft. Sp.-74 sq. ft.	Sh.-245 sq.ft. Bel.-319 sq.ft. Sp.-345 sq.ft.	@ Rs.1.12 @ Rs.1.12 @ Re.0.50	Rs. 274.00 Rs. 357.00 Rs. 172.00 Re. 803.00	1.72
5. Bunwar & kattai leaters	Vegetable	Shoulders & bellies	41.0 59.0	Sh.- 17.0 Kg. Bel.- 25.0 Kg.	Sh.- 106.5 Kg. Bel.- 174.5Kg.	@ Rs.8.50 @ Rs.7.50	Rs. 905.00 Rs.1309.00 Rs.2214.00	4.4 3.9
6. Sole leather	Vegetable	Bellies	113.5	63.5 Kg.	230.4 Kg.	@ Rs.3.25	Rs.749.00	2.24

Sh. - Shoulder, Bel. - Bellies, Sp. - Split.

In case of very heavy hides, however, the yields of bunwar and kattai leathers may be considerably less due to splitting up of the hides. To compensate that the splits are to be properly finished and marketed. Otherwise priority may be given to the production of hydraulic, sole or vegetable crust leathers.

Although hydraulic leather has a moderately good market value the demand for this type of leather is rather limited. It may be pointed out that sole leathers can also be made out of shoulder pieces and the market value of sole leather from shoulders is very close to that of hydraulic leather. In case of scarcity of vegetable tanning materials or in order to meet the demand for shoe upper leather both the shoulder and belly pieces may be finished into upper leather or shrunken grain leather. Upper leathers from these offals have a better market value in India than shrunken grain leathers probably because of the poor demand for shrunken grain leathers in this country. The belly pieces of buffalo hides being rather narrow are not very suitable for shrunken grain leather. Although the marketing potential for this type of leather is much less in India it is not so in other countries where shrunken grain leathers are in good demand. Indian buffalo hides are not uniform in thickness. Practically no utilisable split is obtained from belly pieces but splits are obtained from shoulder pieces. In order to make the upper leather and shrunken grain leather economical these splits should be properly used. There is very little demand for chrome lace leathers at the present moment.

7. <u>Summary and conclusion</u>.

1. A fairly rapid process for the production of vegetable tanned sole leather was adopted and followed in the present study. Physical and chemical properties of the leathers produced by this method were quite comparable with the conventional sole leathers made from Indian buffalo hides.

2. Sole leather making properties of slaughtered buffalo hides collected from slaughter house and fallen buffalo hides

collected from Flaying and Carcass Utilisation Centre from Western India were compared. Similarly, market quality slaughtered hides and market quality fallen hides were collected from hide market in Eastern India and the quantities of sole leathers produced from them were compared.

In both occasions slaughtered buffalo hides were found to be comparatively better in quality than fallen hides. Slaughtered hides were adversely affected due to flay cuts but could be upgraded in quality by trimming off the belly pieces. Fallen hides, besides putrefactive grain damages, were degraded in quality due to the presence of blood marks and stains which became prominent in limed pelt and were retained by the leather even after tanning. Such blood patches were not generally present in slaughtered hides. It was observed that these coloured patches could be removed to an appreciable extent by soaking the hides in an acid soak liquor and liming for a longer period e.g., 7 days.

There was practically no variation in leather yield (when calculated on pelt weight) between the slaughtered and fallen hides. But when calculated on raw weight leather yield was considerably less in fallen hides which was probably due to the presence of more adhering flesh and fat in fallen hides. Area yield of the leathers also did not differ significantly between the slaughtered and fallen hides.

On an average, the qualities of the sole leathers made from slaughtered hides were graded better than the leathers from fallen hides. But selection of the finished sole leathers from fallen hides was found to be roughly proportional to the raw selection of the fallen hides.

There was no difference in abrasion of the leathers but apparent density was slightly higher and the water absorption slightly lower in leathers from fallen hides. But these differences were not very much significant.

3. In an investigation to find out the better utilisation of buffalo hide (45 - 55 lb.) offals it was observed that shoulder and belly pieces could be

conveniently utilised by converting them into bunwar and kattai leathers. The next best proposition appeared to be the production of vegetable tanned sole or crusted leathers. Buffalo hide offals might be finished into corrected grain upper leather if demand exists for such shoe upper leathers or the availability of vegetable tanning materials was inadequate. Shoulder pieces could also be finished into shrunken grain leathers.

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Fig.17: Visual assessment of the qualities of market quality slaughtered and fallen hides as well as the qualities of the leathers produced from them. 1 - First quality, 2- Second quality, 3 - Third quality and R - Rejection quality.

Fig.18: Severe damage in limed pelt caused by faulty flint drying technique

Fig.19: A network of blood marks in limed pelt due to congealed blood

Fig.20: Blood and other coloured patches in limed pelt

Fig.21: A contrast between two sides of the same hide where blood marks are prominent in one side

Fig.22: Presence of blood patches in the side even after pit tanning of the pelt.

NEED FOR ADDITIONAL RESEARCH

Further research work is desired in the following fields:

(i) Interfibrillary materials in hides and skins and their role on the properties of leather

(ii) Better utilization of hide offals

List of publications

1. Effect of locational variation in the hide on processing and properties of chrome tanned upper leather.

   J.K.Khanna, S.C.Nandy and Y.Nayudamma, Symposium on Recent Advances in Mineral Tannages, pp.19,1964

2. Rapid tanning of sole leather using bag tanning technique

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3. ~~Investigations~~ Studies on the qualities of vegetable tanned sole leathers made from slaughtered and fallen hides

   J.K.Khanna, S.C.Nandy, P.S.Venkatachalam and Y.Nayudamma, Leather Science, 13, 191, 1966.

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5. Leather making potentiality of cattle hide obtained from slaughtered and fallen animals - Part-I.

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